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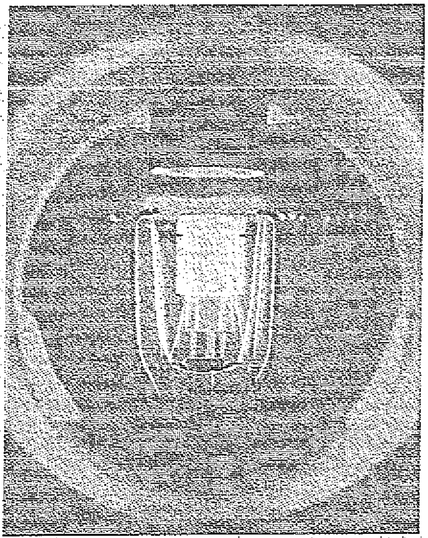
F.W. Froben and L. Singheiser (Editors)

High Temperature Materials Chemistry



Abstracts

International Union of Pure and Applied Chemistry (IUPAC)
Commission: "High Temperature Materials and Solid State Chemistry"

Energietechnik
Energy Technology

Schriften des Forschungszentrums Jülich
Reihe Energietechnik / Energy Technology Volume 10

Forschungszentrum Jülich GmbH
Institut für Werkstoffe und Verfahren der Energietechnik

Klaus Hilpert, Friedrich W. Froben
and Lorenz Singheiser (Editors)

High Temperature Materials Chemistry

Abstracts of the 10th International IUPAC Conference held from 10 to 14 April 2000 at the Forschungszentrum Jülich, Germany.

International Union of Pure and Applied Chemistry (IUPAC)
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Schriften des Forschungszentrums Jülich
Reihe Energietechnik / Energy Technology Volume 10

ISSN 1433-5522 ISBN 3-89336-259-2

Die Deutsche Bibliothek- CIP-Einheitsaufnahme

High temperature materials chemistry: abstracts of the 10th international IUPAC conference, April 10 - 14, 2000, Jülich / Forschungszentrum Jülich GmbH, Institut für Werkstoffe und Verfahren der Energietechnik. Klaus Hilpert ... (ed.). International Union of Pure and Applied Chemistry (IUPAC), Commission: "High Temperature Materials and Solid State Chemistry". - Jülich : Forschungszentrum, Zentralbibliothek, 2000

(Schriften des Forschungszentrums Jülich : Reihe Energietechnik / Energy Technology ; Bd. 10)
ISBN 3-89336-259-2

Publisher and Distributor:	Forschungszentrum Jülich GmbH Central Library 52425 Jülich Germany Phone: +49 (0) 24 61 61 53 68 · Telefax: +49 (0) 24 61 61 61 03 e-mail: zb-publikation@fz-juelich.de Internet: http://www.fz-juelich.de/zb
Cover Design:	Grafische Betriebe, Forschungszentrum Jülich GmbH
Printer:	Grafische Betriebe, Forschungszentrum Jülich GmbH

Schriften des Forschungszentrums Jülich
Reihe Energietechnik / Energy Technology, Volume 10

ISSN 1433-5522
ISBN 3-89336-259-2

Foreword

The HTMC X continues a series of conferences held every two or three years under the sponsorship of the IUPAC. The previous three conferences were held in Orléans (France) 1991, in Vienna (Austria) 1994, and in State College University Park, Pennsylvania (USA) 1997. This time at Aachen (Germany), the organizers bring together the various groups working on fundamental and applied aspects of high temperature materials chemistry. Bridging the gap between fundamentals and technical application will be a major issue of the conference.

The conference will consist of 8 invited lectures, 17 keynote lectures, 41 short oral presentations and about 170 posters. Due to the large number of submitted abstracts, the desire to avoid parallel sessions and the limited time, we were only able to accept a small number of contributions for oral presentation. Therefore, visit the posters – they provide excellent contributions.

Most of the fundamental contributions belong to the fields of thermodynamics, vaporization and solid state diffusion. The emphasis of the technical contributions is on synthesis, high temperature light sources and corrosion. Contributions were submitted from universities, research centres and industry, reflecting the broad scope of the conference. Seven major suppliers of thermodynamic data bases and computer software will present their products and allow hands-on demonstrations. This will give you a unique opportunity for direct comparison of their products.

As in previous conferences, many people have made significant contributions to the success of this conference. The excellent work of the members of the International Advisory Board and the National Advisory Board is highly appreciated, especially for reviewing the large number of papers submitted and for organizing the conference sessions. We also thank the authors of all the contributions to the conference for the high standard of their papers.

April 2000

Klaus Hilpert   F. W. Froben   Lorenz Singheiser

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Defect kinetics in fayalite, Fe_2SiO_4

A82 N. Trofimenko and H. Ullmann; Technical University of Dresden, Germany
Structure-property relations of perovskite-type oxides: Application of Goldschmidt's tolerance factor to highly defective oxides

Coatings

A83 A.D. Shevchenko; Ukrainian Academy of Sciences, Kiev, Ukraine
Coating by copper in the high pressure of the metalloxide HTSC ceramics surface

A84 A.Y. Timoshkin; St. Petersburg State University, Russia
CVD of $A^{III}B^{V}$: gas phase cluster formation.Structures of intermediates and thermodynamics of association processes

A85 Y. Djaoued, P.V. Ashrit et al.; Université de Moncton, Shippagan, Canada
High temperature transformation of sol-gel derived TiO_2 thin films into TiN films

A86 O.V. Demirskaya, T.P. Rebrova et al.;
Institute for Single Crystals, Kharkov, Ukraine
Preparation of ferroelectric films by pyrolysis of metal-organic solutions applied to substrates

A87 C. Metz, G. Wahl et al.; Technical University Braunschweig, Germany
Deposition of protective NiAl coatings on the internal surfaces of tubes

A88 V.M. Danilenko and A.M. Zaslavsky; IPM NASU, Kiev, Ukraine
Theoretical investigation of laser oxides film deposition

A89 A.R. Kaul, O.Yu. Gorbenko et al.; Moscow State University, Russia
Unusual phases and unusual phase equilibria in epitaxial thin oxide films

A90 S. Shalamberidze; The Institute of Stable Isotopes, Tbilisi, Georgia
Pulse laser deposition of boron carbide thin films

Poster Presentations B

Diffusion

B 1 R. Bachorczyk, M. Danielewski and T. Walec;
University of Mining and Metallurgy, Crakow, Poland
Intrinsic diffusivities and diffusion paths in Fe-Ni-Cu alloys

B 2 M. Danielewski, W. Krzyzanski* and R. Bachorczyk;
University of Mining and Metallurgy, Crakow, Poland;
*University of Buffalo, USA
Interdiffusion in multicomponent solid solutions: from diffusional structures in alloys to hyperbolic diffusion

B 3 M. Danielewski, R. Filipek et al.;
University of Mining and Metallurgy, Crakow, Poland
Interdiffusion in oxidised ternary and higher alloys

B 4 R. Bachorczyk, M. Danielewski et al.;
University of Mining and Metallurgy, Crakow, Poland
Intrinsic diffusivities and thermal stability of multicomponent coatings

B 5 S.A. Kuznetsov and M. Gaune-Escard*;
Russian Academy of Sciences, Murmansk, Russia; *CNRS, Marseille, France
Diffusion coefficients of refractory and rare-earth metal complexes in molten salts

B 6 M. Ohtsuka, R. Cremer et al.; RWTH Aachen, Germany
Interdiffusion paths in the diffusion couple Y-Al_2O_3

B 7 E.M. Fryt; Department of Mining and Metallurgy, Crakow, Poland
Properties of TiC at high temperatures

B 8 T. Hehenkamp, R. Kerl and B. Köhler; University of Göttingen, Germany
Formation of equilibrium thermal defects and chemical diffusion in Fe-Al-alloys

B 9 H. Timm and J. Janek; University of Hanover, Germany
Demixing of oxides in a temperature gradient

Synthesis / Reactions

B 10 T. Nagasawa, H. Yamane and M. Shimada; Tohoku University, Sendai, Japan
Synthesis and crystal structure of new oxides in CaO-Y_2O_3-SiO_2 system

B 11 N. Bobrysheva, N. Chezhina and M. Osmolovski;
St. Petersburg State University, Russia
High temperature oxide ceramic materials containing heterovalent magnetic atoms

B 12 A. Baykal, M. Kizilyalli and R. Kniep*; Technical University, Ankara, Turkey;
*Technical University of Darmstadt, Germany
High temperature synthesis of $Sr_3(BP_3O_{12})$

B 13 F.D. Meyer and H. Hillebrecht; University of Bayreuth, Germany
Ternary phases in the system Al/C/N

B 14 F.D. Meyer and H. Hillebrecht; University of Bayreuth, Germany
Ternary phases in the system Al/Si/C

B 15 P. Duerichen and R. Riedel; Technical University of Darmstadt, Germany
Novel precursor derived boron containing silicon carbonitrides: the influence of boron on high temperature stability

B 16 R.A. Andrievski; Russian Academy of Sciences, Moscow, Russia
Nanostructured high melting point compound-base materials: synthesis and properties

B 17 Y.K. Rao and C.H. Raeder; University of Washington, Seattle, USA
Steady-state chemical vapor transport in closed ampoule reactor: measured and predicted growth rates of SnS_2(s) crystals

B 18 O.A. Bilous, M.P. Burka et al.;
National Academy of Science, Kiev, Ukraine
The structure and high-temperature mechanical properties for ternary alloys based on chromium

B 19 X. Zonghuang, L. Yan et al.; University of Beijing, P.R. China
Formation and irradiation-induced optical absorption in MeV boron ion implanted $KNbO_3$ optical waveguides

B 20 S. Okada, K. Kudou* et al.; Kokushikan University, Setagaya, Japan *Kanagawa University, Yokohama, Japan
Crystal growth and structure of Nb_5Sn_2Ga by metal tin solutions and properties of the crystals

B 21 S. Ranganathan, A.N. Bhagat* et al.; National Metallurgical Laboratory, Jamshedpur, India; *Tata Steel, Jamshedpur, India
Experimental investigations and thermodynamic prediction of the formation of complex precipitates during high temperature processing of high strength low alloy steels

B 22 P. Saewong, K. Sujirote and P. Thavorniti;
National Metal and Materials Technology Center, Bangkok, Thailand
A study of SiC fabrication from rice husk and its ash by Acheson process

B 23 S. Shalamberidze, G. Kalandadze et al.;
Institute of Stable Isotopes, Tbilisi, Georgia
Some peculiarities of sintering of boron and boron carbide

B 24 Binbo Wei; Northwestern Polytechnical University, Xian, P.R. China
Undercooling phenomenon and rapid solidification of liquid metals and alloys

Modelling

B 25 V.L. Vinograd, A. Putnis and [illegible] of Münster, Germany
Description of Al,Si orde [illegible] using the cluster variation method

WITHDRAWN

B 26 P. Koukkari and K. Penttilä; VTT Chemical Technology, Finland
Coupled thermodynamic and kinetic models for high temperature processes

B 27 B. Hallstedt and L.J. Gauckler; ETH, Zürich, Switzerland
Thermodynamic modelling of oxide solid solutions and melt processing of Bi-2212 superconductors

B 28 G. Zhang and O. Ostrovski;
University of New South Wales, Sydney, Australia
Kinetic modeling of synthesis of titanium carbide

B 29 E.B. Rudnyi; Moscow State University, Russia
Taking into account systematic errors during simultaneous assessment of materials properties

B 30 M. Sukiennik and K. Gargul;
University of Mining and Metallurgy, Crakow, Poland
The problem of properties modeling in associated solutions

B 31 L.N. Gorokhov and I.V. Sidorova;
Glushko Thermocenter of RAS, Moscow, Russia
Enhanced volatilization of uranium dioxide in presence of water vapor

B 32 J.A. Golczwski, H.J. Seifert and F. Aldinger; MPI Stuttgart, Germany
A thermodynamic model of amorphous grain boundary phase in liquid-phase sintered β-SiAlON ceramic

B 33 A.L. Udovsky and M.V. Kupavtsev*; Russian Academy of Sciences; Moscow, Russia;*Physical Technical University, Moscow, Russia
The computer realization of U-algorithm of thermodynamic calculation of isothermal sections of phase diagrams of ternary systems. Application to the Ni-Al-W system

B 34 N.E. Dubinin, V.V. Filippov* and N.A. Vatolin; Academy of Sciences, Ekaterinburg, Russia; *Ekaterinburg Artillery Institute, Russia
Square-well fluid as a reference system in variational method

B 35 T.V. Trefilova and N.E. Dubinin;
Russian Academy of Sciences, Ekaterinburg, Russia
Investigation of the binary liquid metal alloys thermodynamics using ORPA and theoretical dependence of pseudopotential parameter from alloy composition

B 36 V.A. Gorelski and V.V. Kim; Tomsk State University, Russia
Numerical modeling of the possibility of gasless detonation in the system CuO+B under shock-wave leading in three dimensional statement

B 37 H. Yokokawa, N. Sakai et al.;
National Institute for Materials and Chemical Research, Ibaraki, Japan
Generalization of chemical potential diagrams and its application to high temperature materials chemistry

Thermodynamics

B 38 O.Y. Pankratova, R.A. Zvinchuk and A.V. Suvorov;
St. Petersburg State University, Russia
Thermochemistry of non-stoichiometric titanium selenides and tellurides

B 39 B. Blachnik and E. Klose; University of Osnabrück, Germany
Calorimetric study of liquid alloys and pathways of reactions in the system Bi-Sb-Se

B 40 V.P. Zlomanov, A.Yu. Zavrazhnov* et al.;
Moscow State University, Russia; *Voronezh State University, Russia
Manometric method in scanning the phase diagrams of low volatile Gallium chalcogenides using the auxiliary compounds

B 41 R. Kainuma, Y. Inohana et al.; Tohoku University, Sendai, Japan
Partition of alloying elements between γ(A1) and δ(Ni_3Nb:D0a) phases in the Ni-Fe-Cr-Nb base systems

B 42 D.N. Kagan, G.A. Krechetova and E.E. Shpilrain;
Russian Academy of Sciences, Moscow, Russia
Gibbs energy and enthalpy of formation for ternary alkali metal alloys at temperatures up to 1200 K

B 43 V. Goryacheva, I. Kutsenok et al.; Moscow State University, Russia
Thermodynamic functions of amorphous alloys Co-Si-B

B 44 B. Onderka, T. Pomianek* et al.; Polish Academy of Science, Crakow, Poland;
*University of Technology, Rzesnów, Poland
An experimental study on thermodynamics of Cu-As liquid solutions

B 45 G.F. Voronin; Moscow State University, Russia
Prediction of thermodynamic properties and stability for solid chemical compounds

B 46 V.L. Cherginets, O.V. Demirskaya and T.P. Rebrova;
National Academy of Sciences, Kharkov, Ukraine
On relative oxoacidic properties of the eutectic melt $BaCl_2$-KCl-NaCl (0.43:0.29:0.28) at 700°C

B 47 T.N. Kol'sova, G.D. Nipan and K.S. Gavrichev;
Russian Academy of Sciences, Moscow, Russia
Solid solutions in the Y_2O_3-BaO-WO_3-CuO system

B 48 H. Flandorfer, C. Luef and H. Ipser; University of Vienna, Austria
The In-Pd-Sb phase diagram

B 49 W. Gasior, Z. Moser et al.; Polish Academy of Sciences, Crakow, Poland
Thermodynamic properties and the phase diagram of Al-rich part of Al-Si-Cu system

B 50 D. Labroche, J. Rogez* et al.; CEA, Pierrelatte, France; *CTM, Marseille, France
Thermodynamic and structural characterization of the $UFeO_4$ and U_3FeO_{10} compounds

B 51 M.A. Turchanin, I.V. Belokonenko et al.;
Donbass State Mechanical Engineering Academy, Kramatorsk, Ukraine
Enthalpies of formation of liquid binary Ni + (Ti, Zr, and Hf) alloys

B 52 N. Shelkova, A. Zaitsev and B. Mogutnov; I.P. Bardin Central Research Institute for Metal Physics and Functional Materials, Moscow, Russia
Physical and chemical properties and structure of metal-non metal high temperature solutions

B 53 P. Franke; RWTH Aachen, Germany
Thermodynamics and defect chemistry of mixed oxides with spinel structure

B 54 L.N. Gorokhov, G.A. Bergman et al.;
Glushko Thermocenter of RAS, Moscow, Russia
Thermodynamic properties of lanthanide triiodides in condensed and gaseous states

B 55 L.C. Prasad and A. Mikula; University of Vienna, Austria
Effect of temperature on the surface properties of Cu-Sn liquid alloys

B 56 H. Näfe, F. Meyer and F. Aldinger; MPI Stuttgart, Germany
Electrochemical characterization of the equilibrium between Na-β and Na-β''-alumina as a function of the phase composition

B 57 S. Tanasescu, N.D. Totir et al.;
Institute of Physical Chemistry, Bucharest, Romania
High temperature thermodynamic data of the Ca- and Sr-doped $LaMnO_3$

B 58 S. Tanasescu, N.D. Totir et al.;
Institute of Physical Chemistry, Bucharest, Romania
A comparative study of the influence of compositional variables on the thermodynamic properties in the substituted lanthanum manganites

B 59 T.Ya. Velikanova, E.L. Semenova and T.G. Mazhuga;
Academy of Sciences of Ukraine, Kiev, Ukraine
The Ti-Ni-Os ternary system

B 60 O.I. Dovbenko, A.A. Bondar and T.Ya. Velikanova;
Academy of Sciences of Ukraine, Kiev, Ukraine
The regularity in constitution of phase diagrams for the ternary systems formed by chromium and carbon with d-metals of V group

B 61 V.M. Danilenko, A.A. Rubushevsky and T.A. Velikanova;
National Academy of Science, Kiev, Ukraine
Thermodynamical evaluation on phase equilibria in Fe-Mo-Cr system

B 62 L.V. Goncharuk, V.G. Khorujaya and V.R. Sidorko;
National Academy of Science, Kiev, Ukraine
Thermodynamic properties of alloys of scandium with iridium

B 63 R. Kesri, A. Adnane and S. Hamar-Thibault*;
Laboratoire de Métallurgie Structurale, El Alia Alger, Algier, Algeria; *ENSEEG, Saint Martin d'Hères, France
High temperature equilibria in iron rich FeVCuC alloys

B 64 S.I. Lopatin; St. Petersburg State University, Russia
Regularities of vaporization behaviour of oxyacid salts

B 65 K. Korniyenko*, A. Leithe-Jasper**, P. Rogl et al.;
University of Vienna, Austria;
*Institute of Problems of Materials Science, Kiev, Ukraine;
**Natl. Institute for Research in Organic Materials, Tsukuba, Japan
Constitution of the ternary systems Nb-B-C and Mo-B-C

B 66 A. Yassin and R. Castanet*; University of Baghdad, Alm-Jadriyah, Iraq; *CNRS, Marseille, France
Critical review limiting partial enthalpies of elements in liquid tin

B 67 M. Yurechko, B. Grushko and V. Shemet; Forschungszentrum Jülich, Germany
Phase equilibrium in the Al-rich part of the Al-Pd-Co alloy system

B 68 A.F. Maiorova, S.N. Mudretsova et al.; Moscow State University, Russia
Thermal properties of rare-earth manganites with colossal magnetoresistance

B 69 A. Ciccioli, G. Balducci and G. Gigli; University of Rome, Italy
The stability of the PdX molecules (X=groups IIIA and IVA elements)

Corrosion

B 70 C. Konetschny and R. Riedel; Technical University of Darmstadt, Germany
High temperature properties of polymer derived amorphous Si-C-N materials

B 71 H. Klemm, C. Schubert and W. Hermel; Fraunhofer-Institute, Dresden, Germany
High temperature oxidation of non-oxide silicon based ceramics

B 72 E.H. Edwin, T. Arnesen et al.; Statoil R&D, Trondheim, Norway
Carburization test method tailored for ethylene cracker tubes

B 73 C. Bertrand, A.L. Daltin et al.; Université de Reims, France
Comparative study of the reaction of copper-nickel alloys (electrodeposited and rolled) at high temperatur in pure oxygen

B 74 E. Butchereit and K.G. Nickel; Univers[illegible]ngen, Germany
The control of the hig[illegible]ion behaviour of precursor derived Si-B-C-N cera[illegible] pre-treatments?

WITHDRAWN

B 75 V.Ya. Kudyakov, A.E. Domnin et al.;
Institute of High Temperature Electrochemistry, Ekaterinburg, Russia
High temperature electrochemical corrosion of steel 12Kh18Ni10Ti and its components in alkali carbonate melts at 500-650 °C

B 76 A. Ralison, F. Dettenwanger and M. Schütze; Dechema, Frankfurt, Germany
Oxidation of orthorhombic TiAlNb alloys at 800°C in air

B 77 U. Koops and M. Martin; Technical University of Darmstadt, Germany
High temperature corrosion of cobalt based intermetallic compound CoGa

B 78 N.S. Jacobson, D. Myers* and D. Zhu**;
NASA Research Center, Cleveland, USA; *East Central University, Ada, USA;
**Ohio Aerospace Institute, Brookpark, USA
Rhenium-oxygen interactions at high temperatures

B 79 Y. Ogura, M. Kondo et al.; Mitsubishi Heavy Industries, Yokohama, Japan
Oxidation behavior of Y_2SiO_5/SiC coating for C/C composites

B 80 K.-H. Hinssen, A.-K. Krüssenberg* et al.; Forschungszentrum Jülich, Germany;
*Forschungszentrum Rossendorf, Germany
Oxidation of innovative carbon based materials for future energy systems

B 81 M. O'Reilly, J. Corish and R.J. Fordham*; Trinity College, Dublin, Ireland;
*European Commission JRC, Petten, The Netherlands
The effects of exposing hot pressed silicon nitride and rare earth silicon oxy-nitride phases to a high temperature H_2S rich gas environment

B 82 M. Makipaa and R.J. Fordham; JRC Petten, The Netherlands
Stability of some potassium and sodium ferrites in relation to chloride-enhanced oxidation

B 83 T. Karwath, P. Biedenkopf et al.; Forschungszentrum Jülich, Germany
High temperature corrosion of ceramics against coal slags

Post Deadline Posters C

Assigned to and displayed together with Posters A 9 – A 36
"Vaporization / Mass Spectrometry /Temperature Measurement"

C 1 D. Labroche, J. Rogez* et al.;
CEA-VALRHO, Pierrelatte, France; *CTM, Marseille, France
New thermodynamic measurements and assessment in the U-Fe system

C 2 J. Svoboda and J. Sopoušek*; Academy of Sciences of the Czech Republic, Brno, Czech Republic; *Masaryk University, Brno, Czech Republic
Simulation of kinetics of ferrite growth in Fe-C austenite with interface of finite mobility

C 3 R.I. Sheldon, G.H. Rinehart et al.; Los Alamos National Laboratory, USA
The optical properties of liquid cerium at 632.8 nm

C 4 G. Meloni and K.A. Gingerich; Texas A&M University, College Station, USA
Bond energies of ternary transition metal carbides from mass spectrometric equilibrium measurements

C 5 K.A. Gingerich, R.W. Schmude, Jr., J.E. Kingcade, Jr., and G. Meloni;
Texas A&M University, College Station, USA
Knudsen-effusion mass spectrometry study of tin clusters: Sn_2 -Sn_7

Assigned to and displayed together with Posters B 9 – B 24
"Synthesis /Reactions"

C 6 G. Krabbes; University of Dresden, Germany
High temperature reactions for controlling the low temperature properties of $REBa_2Cu_3O_7$ based superconducting ceramics

Invited Lectures

I1 – I8

HYDROCARBON OXIDATION HIGH TEMPERATURE CHEMISTRY

J. Warnatz
Interdisziplinäres Zentrum für Wissenschaftliches Rechnen (IWR)
Universität Heidelberg, Im Neuenheimer Feld 368, D-69120 Heidelberg

The exact knowledge of the hydrocarbon oxidation kinetics is very important due to the fact that this process is involved in many technological processes: combustion in engines and furnaces, flame synthesis of materials, partial oxidation processes in chemical technology, catalytic combustion and exhaust gas treatment, etc. The paper will give an overview on the present state of the art with respect to kinetic data on gas-phase and surface oxidation of hydrocarbons. Furthermore, some applications are described in the areas mentioned above.

Gas-phase oxidation of hydrocarbons: Examples here are (1) combustion in engines and furnaces, where the purpose is optimum combustion efficiency and minimization of the formation of pollutants like soot and nitrogen oxides, and (2) partial oxidation processes in industrial chemical reactors, where cheap natural gas is transformed into high-value partially oxidized hydrocarbons like alcoholes, aldehydes, alkene oxides, etc.

Surface oxidation of hydrocarbons: Examples here are (1) catalytic combustion which leads to NO-free exhaust gas due to the absence of O atoms and CH radicals in the gas phase, (2) exhaust gas treatment like by the three-way catalyst for gasoline engines and lean DeNOx for direct-injected Diesel and Otto engines.

Combined use of gas-phase and surface mechanisms: In many applications, both gas-phase and surface chemistry is taking place. Examples here are (1) flame generation of diamond, where deposition species like C atoms and CH_3 radicals are formed in gas-phase combustion and, after transport to the surface, are used to build up the diamond lattice, (2) syngas generation, where heterogeneous processes are predominant at atmospheric pressure, but gas-phase chemistry is becoming important at high pressure demanded in industrial reactors.

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Application of Very High Temperature Mass Spectrometry to Vapor Pressure Determinations Over Liquid Refractories

J. W. Hastie, D. W. Bonnell and P. K. Schenck
NIST, Gaithersburg, MD, USA

Existing thermodynamic and vaporization data for liquid refractories is based either on estimates or on data extrapolated from lower temperature studies on the solids. Previously, we and others have shown that pulsed laser heating, coupled with time-dependent mass spectrometry, can be used for semi-quantitative measurements of vaporization thermochemistry. The present work extends this approach with more direct and more accurate determinations of the system temperature and pressure, and of key determining factors such as ionization cross sections, in addition to the nature of the gas dynamic expansion and thermal equilibration processes.

Example material systems considered include Al_2O_3, $BaTiO_3$, SiC, and ZrO_2-7%Y_2O_3, at temperatures and pressures typically in the range of 3000-5000 K and 0.1-10 bar, respectively. These systems exemplify both congruent and non-congruent vaporization behavior. Key improvements in the measurement approach include: (a) direct spectroscopic time-dependent temperature determinations, based on Planck's-law radiation behavior, (b) indirect temperature determinations, based on time-of-flight velocity distribution measurements, (c) ionization cross section verification using system stoichiometry and (d) pressure calibration using insitu deposition rate and flux spatial distribution measurements. As may be expected, significant differences are found between literature estimated or extrapolated pressures and those directly observed in the present study. The most significant factors contributing to these differences appear to be a lack of heat capacity data for the liquids and spectroscopic and ionization cross section data for the vapor species.

Properties of High Temperature Melts Using Levitation

Paul C. Nordine, Containerless Research, Inc., 906 University Place, Evanston, IL USA 60201

Levitation techniques are useful tools for high temperature melt property studies. They eliminate the problem of reaction with containers and allow deep undercooling of melts. The containerless conditions may be obtained by opposing gravity with a levitation force, in a transient experiment performed faster than any influence of gravity, or allowing an entire experiment to free-fall. This paper addresses these methods and results of recent research using containerless techniques. The low-gravity environment of an orbiting laboratory enable many new experiments that have not been possible via earth-based levitation.

Ellipsometry and radiation pyrometry yield the spectral emissivity and optical properties, and the true temperature of levitated liquids. Surface tension and viscosity are measured by observing resonant oscillations of liquid drops, or from drop shape relaxation rates. X-ray scattering experiments yield liquid structure. Electrodeless electrical conductivity measurements were recently demonstrated for liquid Al_2O_3, Si, and Ge. Phase equilibria, including melting points and liquidus temperatures can also be measured with containerless techniques. Microsecond pulse heating can yield thermophysical properties at temperatures up to the critical point.

New and unusual phenomena and processes have been explored in studies of undercooled melts. For example, depending on process conditions, undercooled molten $Y_3Al_5O_{12}$ may (i) crystallize to form YAG crystals, (ii) form a non-equilibrium mixture of crystalline phases, (iii) undergo a liquid-liquid phase transition, (iv) be cooled to form a bulk sample of YAG-composition glass, and (v) be pulled into glass fibers. Highly non-Arrhenian viscosity vs temperature behavior (fragile liquid behavior), glass formation, and the critical cooling rates required to avoid crystallization and obtain a glass have been determined for many new oxide materials. The increased viscosity of undercooled melts has allowed fiber pulling from undercooled melts and the synthesis of glass fibers, with properties not available in silica-based glasses.

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Thermodynamic Modelling

Mats Hillert
Dept. Materials Science, KTH
SE-10044 STOCKHOLM, Sweden

In order to store thermodynamic data for later retrieval and use in thermodynamic calculations, it is necessary to use analytical descriptions based on models. A great spectrum of models are available ranging from the simple regular solution model to very sophisticated descriptions based on the detailed physics of the system. For practical purposes it may be advantageous to use as general a model as possible, applicable to a great number of types of phases. The Compound Energy Model may have such qualities and its application to various types of solution phases will be described. Practical examples will be presented.

The Compound Energy Model can describe long-range order. The incorporation of a quasi-chemical approximation of the effect of short-range order will also be discussed.

Transport processes in metal halide gas discharge lamps

W. van Erk

Philips Lighting BV, building EEA-4, P.O. box 80020,

5600JM, Eindhoven, The Netherlands

Metal halide gas discharge lamps are increasingly being used in all kinds of application areas such as motor car head lights, accent lighting in shops, indoor and outdoor sports, studio, theater, and disco lighting, and for projection purposes. These lamps are selected for their high efficiency, potential for long life, and compact size which is important for focussing the light into narrow beams. The light is created by a mercury vapour discharge to which metal halides are added to obtain the desired spectrum. The discharge runs between tungsten electrodes and is contained in a quartz glass or polycrystalline alumina vessel. Temperatures involved in the operation of such a light source are high: the coldest spot on the vessel wall is readily 1000 K and the top temperature of the electrodes can be as high as the melting temperature of tungsten (3695 K). These high temperatures and large temperature gradients, in combination with the presence of corrosive compounds like metal halides, lead to complex transport phenomena which make it difficult to comply with lamp requirements such as good maintenance of light technical properties and a long lamp life.

In this contribution the following subjects will be discussed:

- Processes at the coldest spot of the vessel: Here the excess of metal halides will condense, usually forming a molten salt pool. Complex formation both in the melt and in the gas phase can have strong impact on the vapour pressures of the various metal halides. Scandium and rare-earth metal halides will react with the vessel wall thus forming silicon or aluminum halides. Furthermore, wall material may dissolve in the salt pool.
- Transport along the vessel wall: This leads to blurring of the initially transparent glass. Most likely gas phase transport of quartz glass causes the roughening of the surface.
- Transport to the electrodes: Elements like Si, Fe, Al, Hf,.. tend to dissolve into tungsten at high temperatures.
- Transport from the electrodes: Tungsten transport can cause blackening of the vessel wall.

Thermodynamic modeling assuming local chemical equilibrium can be very helpful in understanding these transport processes. However, especially for heterogeneous reactions, kinetic effects may dominate. Furthermore the availability of reliable data regarding pure compounds and mixed phases remains a prerequisite.

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Reactions of Hot and Cold Metal Clusters

Vladimir E. Bondybey
Technische Universität München, Institut für Physikalische und Theoretische Chemie,
Lichtenbergstr. 4, 8046 Garching, Germany

Reactions of metal ions and ion clusters, and in particular those of transition metals, were studied extensively by mass spectroscopy, with the results being often exploited to draw conclusions about the metal catalytic activity. Often overlooked in interpretating the results are the effects of temperature. The interaction energies of many compounds with a metal surface, particularly when it is charged are often quite large. While at high pressures, or in the case of a solid surface this interaction energy is readily dissipated into the surrounding medium, in the high vacuum environment of a mass spectrometer the energy has to be dissipated within the collision complex, if this is to be stabilized. A simple examination shows, that the temperatures of such a small $M_n + R$ complex, (where M is metal and R is its collision partner - e.g. ethylene or benzene) may be quite high, and for small n ($n<10$) easily exceed 1000 K. For a meaningful interpretation of the results this temperature rise has to be taken into consideration. This temperature rise also has a decisive influence on whether the complex between the undecomposed reactant and the ionic cluster is stabilized, or whether a further reaction with ligand decomposition and metal carbide, oxide or nitride formation takes place. In the present talk, a number of examples of this effect will be discussed, and the reactions of "hot" metal anion or cation clusters will be compared with those of truly cold species.

Chemical Kinetics at Solid/Solid Interfaces

H. Schmalzried

The kinetics of solid/solid interfaces controls in part the course of heterogeneous reactions in the solid state. In this presentation, the essential kinetic situations of interface kinetics in solids are defined and the basic formal considerations are summarized. In addition to the role of interfaces as resistances for transport across them, they offer high diffusivity paths laterally and thus represent two-dimensional reaction media.

Experimental examples will illustrate kinetic phenomena at static and moving phase boundaries, which include problems concerning exchange fluxes, boundary controlled solid state reactions, interface morphology, nonlinear phenomena connected with interfaces and reactions in boundaries.

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High Temperature Chemical Vapor Deposition, an Effective Tool for the Production of Coatings

G. Wahl
Insitut für Oberflächentechnik und plasmatechnische Werkstoffentwicklung
Technische Universität Braunschweig
Bienroder Weg 53
38108 Braunschweig

CVD Processes have a large throwing power and can operate at atmospheric pressure. Therefore they are for many applications very economical. High temperature CVD processes are in addition very useful. because the crystal structure can be controlled over a very large range (eg. epitaxial layers or other special layer structures) and because high temperature diffusion processes are connected with the layer growth. Therefore diffusion layers can be produced.

The following applications of high temperature CVD are described:

1) Deposition of perowskites which are used for the membrane technology, for super-conductors and as magnetoresistive material
2) Deposition of Yttrium stabilized $ZrO2$ layers as ion conductors and heat barrier coatings
3) Deposition of aluminide coatings in long tubes for corrosion protection
4) Deposition of $MoS2$ - TiN Dispersion coatings as low friction material
5) BN deposition on fibers for fiber reinforced materials.

The special properties of the coatings are discussed and the processes are simulated with the aim to facilitate the scale up of the processes. For the simulation the computer code Fluent was used.

Keynote Lectures

K 1 – K 17

Ceramic Materials in a Pressurized Coal Combustion Process – A Survey

M. Förster; STEAG, Dorsten, Germany

Abstract will be distributed at the Conference.

K2

Molecular Beam Sampling, Mass Spectrometric Detection of Inorganic Species Released During Biomass Thermochemical Conversion

David C. Dayton and Thomas A. Milne
National Renewable Energy Laboratory
Chemistry of BioEnergy Systems Center
1617 Cole Boulevard, MS 3311
Golden, CO 80401-3393

Combustion, gasification, and pyrolysis are all potential processes for producing electricity from biomass. The fate of the alkali metals and other inorganic species initially present in biomass during each of these processes can affect the success and efficiency of electricity production. Alkali metals, in particular potassium, have been implicated as key species for enhancing fouling and slagging of heat transfer surfaces in power generating facilities that convert biomass to electricity via direct biomass combustion. When biomass is used as a fuel in boilers, the deposits formed reduce efficiency, and in the worst case, lead to unscheduled plant downtime. The fate of alkali metals and other inorganic species released during biomass combustion, gasification, and pyrolysis has been studied by directly sampling the hot gases liberated from combustion and gasification of small biomass samples in a variable-temperature quartz-tube reactor. Several molecular beam mass spectrometer (MBMS) systems, two single quadrupole systems, one triple quadrupole system, and a photoionization time-of-flight mass spectrometer system, are available for monitoring these high temperature, bench-scale processes. Results collected with each of these systems will be presented.

We have successfully used the MBMS technique to identify alkali species released during the combustion of numerous biomass feedstocks, black liquor solids and chars, coal, and blends of biomass and coal. The results of these laboratory studies indicate that during biomass combustion, initial feedstock composition has the most pronounced effect on alkali metal released during combustion. Four mechanisms of alkali metal release involving potassium sulfate, potassium chloride, potassium hydroxide, and potassium cyanate have been identified depending on the feedstock composition. Sodium is the most abundant alkali metal in black liquor, a major residue from the Kraft pulping process, and corresponding sodium species are observed during black liquor combustion and gasification. New areas of interest include 1) using low energy (10.5 eV) photoionization in conjunction with a molecular beam sampling, time-of-flight mass spectrometer to minimize fragmentation of detected inorganic and organic products, 2) studying the thermochemistry of heavy metal species with particular emphasis on chromium species, 3) studying the release of heavy metals during solid fuel combustion, and 4) developing a continuous feed, entrained-flow reactor to study kinetic rates of organic and inorganic species released during solid fuel thermochemical conversion.

Thermodynamics of Ceramic Systems

H. J. Seifert
Max-Planck-Institut für Metallforschung and
Institut für Nichtmetallische Anorganische Materialien, Universität Stuttgart
Pulvermetallurgisches Laboratorium
Heisenbergstr. 5, D-70569 Stuttgart, Germany

Microstructure tailoring of high-component ceramic materials requires careful controlling of a large variety of physico-chemical sintering parameters. One of the most important fundamentals to understand the reaction and diffusion paths occuring during the ceramic sintering process is the knowledge of the thermodynamic equilibrium states. A modern way to provide such knowledge is the combination of computer CALculation of PHAse Diagrams (CALPHAD) with directed experimental studies. Anaytical thermodynamic descriptions for the different phases establishing the ceramics microstructure have to be developed. The sublattice models used are closely oriented to the structure of the liquid and solid phases, respectively. The treatment of oxides (e.g. silicates, aluminates, spinel phases), nitrides and oxinitrides (e.g. SiAlON-phases) requires the careful selection of dependent and independently adjustable thermodynamic model parameters. The selection criteria will be discussed.

The binary and ternary thermodynamic data are stored in computer databases and are used for extrapolating calculations of phase equilibria, phase reactions and thermodynamic functions of multicomponent ceramics systems not previously subjected to experimental investigation. To check these results well defined key experiments require thermal analysis (DTA/TG, dilatometry), calorimetry and X-ray diffractometry at temperatures higher than 800 °C, respectively. The data are also used to refine the datasets.

Depending on the specific demand, tables or graphical representations, e.g. phase diagrams, property diagrams or phase composition diagrams maybe chosen. From these data favourable green body compositions and sintering regimes can be derived. The specific features of the thermodynamic assessment of ceramic systems and the link to application oriented problems will be illustrated by the modelling of oxides (e.g. spinel phases, rare earth aluminates, Al-titanate) and non-oxide ceramics (Si_3N_4-, SiC-related systems), respectively.

K4

HIGH TEMPERATURE MASS SPECTROMETRIC STUDY OF OXIDE MELTS

V. L. Stolyarova

Institute of Silicate Chemistry of the Russian Academy of Sciences,
ul. Odoevskogo 24 korp. 2, 199 155 St. Petersburg, Russia

Vaporization processes and thermodynamic properties of oxide melts have the important role in the various fields of high temperature technologies. Comparison of the available thermodynamic properties of the binary borate, silicate, germanate and phosphate melts studied by the high temperature mass spectrometric method is carried out from the point of view of acid-base concept. The question on the reliability of the experimental data is considered compared with the values obtained by various mass spectrometric approaches and found by various techniques of high temperature chemistry such as the electromotive force method, high-temperature calorimetry of solutions, method of exchange equilibria in slags.

The deviations from the ideality of the B_2O_3, SiO_2, GeO_2 and P_2O_5 chemical potentials as a function of the content of oxide modifier in the series of the binary systems are in agreement with the variety of vaporization processes of their components, such as dissociation, association and polymerization. The following parameters were taken into account to understand and to predict the vaporization character of the binary oxide melts according to the position of oxide modifier in the Periodic table: values of the differences of electronegativities, forming oxides; enthalpy of formation of oxide modifier; the lattice energy of the oxide modifier per mole O^{-2}; the energies of the M-O-X bond (X= P, B, Si, Ge).

Modeling and Experimental Studies on the Effect of Thermophysical Properties on Field-Activated Combustion Synthesis Reactions

Zuhair A. Munir
Department of Chemical Engineering and Materials Science
University of California, Davis, CA 95616, USA

On the basis of a modified Fourier heat balance relationship, modeling studies were conducted to determine the effect of thermal and electrical conductivites and relative density on wave propagation in field-activated self-sustaining reactions. Electrical conductivity plays a major role in the localization of the current, and hence the degree of activation by the field. Systems with high conductivity products have a constant degree of activation and wave velocity. In contrast, in systems with low conductivity products, the velocity decreases with time, leading to the extinction of the wave in some cases. Experimental observations are in qualitative agreement with the modeling work.

For thermal conductivity, the modeling work shows the existence of an optimum value: higher values lead to extensive thermal diffusion and low values lead to insufficient heat transfer to cause ignition. In both cases, the velocity of the wave is low. These results provide explanation for the observed dependence of wave velocity on the relative density of reactants in self-sustaining reactions. Modeling and experimental studies showing the effect of an electric field on this dependence are presented and discussed.

K6

Surface Tension Modeling of Melts*

Qiao Zhiyu, Yan Lijun, Xie Yunan, Zhanmin Cao
Dept. of Physical Chemistry
University of Science & technology Beijing
30 Xueyuan Lu, Beijing 100083, P.R.China

The surface tensions of pure liquid metals and inorganic compounds estimated by using artificial neural network (ANN) method.

Based on Butler's original treatment with special attention to model parameter (and thermodynamic parameters of liquid bulk phase, the surface tensions of liquid alloys, molten mattes and salts mixtures are predicted by using a well designed computer program with C++ language, named STCBE (Surface Tension Calculation based on Butler Equation). The agreement between calculated values and experimental data is good enough.

The surface tensions of ternary melts are also predicted from those of binary boundary systems by use of geometric models and a general solution model. The predicted results also agree well with experimental data.

The prediction of surface tensions of undercooled liquid alloys is discussed and some calculated results of undercooled liquid alloys are given as examples.

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* Project supported by National Natural Science Foundation of China

K7

DEFORMABLE CLUSTER MODELLING IN ALLOY THERMODYNAMICS.

W.A. Oates,
Science Research Institute,
University of Salford,
Salford M5 4WT,
U.K.

Effectively all solution models which are used in the empirical assessment of the thermodynamics of alloys are constant volume models, whereas the experimental results refer to constant pressure conditions. There are often significant volume changes occurring within and between phases and it is desirable that models take cognizance of this fact. The material to be presented will demonstrate how the use of deformable cluster modelling, in conjunction with the cluster/site entropy approximation, can explain several features found in real systems which cause great difficulty for constant volume models.

K8

Atomic Structure of High Temperature Oxide Melts

S. Krishnan
Containerless Research, Inc., Evanston, IL, USA

This article will describe recent experimental studies of the atomic structure of high temperature oxide melts in their normal and supercooled states. Structural results on liquids these oxide melts were obtained with the aid of synchrotron x-ray scattering on levitated liquid materials over a wide temperature range, from about 1000-3500K. X-ray diffraction and anomalous x-ray scattering methods have been employed. Results on liquid aluminum oxide shows that it undergoes a drastic structural change upon melting with the Al coordination changing from octahedral in the solid to tetrahedral in the liquid. Further, as the liquid is supercooled, there is a small increase in the intermediate-range order as expected from the known temperature dependence of viscosity of liquids. Results on yttrium oxide show that at temperatures in excess of the melting point, the first two coordination shells merge, indicative of increased ionicity. Supercooling results in a sharpening and strengthening of the first two peaks in the S(Q) and G(r) values together with a decrease in coordination and an increase in the Y-O distance. Results will also be presented on recent studies on YAG and mullite which are mixtures of alumina and yttria , and alumina and silica, respectively. These latter results will show the evolution of liquid structures in pseudo-binary oxide mixtures. The results will also be discussed in the context of other structural studies and known physical properties of these oxide melts.

The Thermochemistry of NaI/LiI/DyI3 Molten Salt, Vapor Equilibria

Joseph A. Baglio and Charles W. Struck
Research and Development
OSRAM SYLVANIA
71 Cherry Hill Drive, Beverly MA 01915

The intensity of light emission and the color of metal halide based light sources depend on the absolute concentrations of the alkali, metal trihalides and other additives to the arc tube. Complexing (chemical transporting) agents are used to increase the vapor pressures of the metal trihalides at a given temperature and/or to lower the arc tube temperature in order to decrease corrosion reactions between the metal iodide components and the wall of the arc tube. The vapor pressures are, however, dependent on the creation of vapor complexes and the activities of all the components in a melt.

In order to describe the vapor composition throughout the compositional range of a melt of interest one needs thermodynamics descriptions of the vapor species and of all condensed species including the multi-component molten salt. In order to model systems such as NaI/LiI, NaI/ScI_3, and LiI/ScI_3 we used, in addition to the NaI/ScI_3 and NaI/LiI phase diagrams, our knowledge of the vapor pressures of ScI_3, NaI, LiI species as well as the $NaScI_4$ and $LiScI_4$ complexes above the pure components and above the melts.

We will present our strategy, which we call the Multi Species Melt Model, for obtaining our descriptions of the NaI/LiI, NaI/ScI_3 and LiI/ScI_3. and the combined NaI/LiI/ScI3 molten salt systems. In addition we compare the vapor pressures calculated using our models to those obtained from the literature. This comparison gives a measure of the accuracy that one can expect both from experimental and modeling work.

The advantage of using our MSMM is that it systematizes estimating the activities of all the species in a molten salt. We describe the molten salt as an ideal mixture of liquid species which have a relationship to the structure of the melt. In addition, the procedures used to obtain the thermodynamics descriptions of the scandium iodide based melts can be applied to the rare earth and other melt systems of interest to lighting research.

K 10

The Meaning of "Structure" for Metal Halide Molecules

Magdolna Hargittai

Structural Chemistry Research Group of the Hungarian Academy of Sciences, Eötvös University, Pf. 32, H-1518, Budapest, Hungary

Metal halides are intriguing systems. On the one hand, they have very simple molecular and structural formulae, on the other hand, they pose real challenges even for today's sophisticated structure-determination techniques.

By the structure of a metal halide molecule we mean the structure of free molecules, which also means vapor-phase systems, under high-temperature conditions in most cases. This is the structure that the experimental techniques determine. In addition to experimental work, today computational techniques are being increasingly utilized for the determination of these structures. Alas, the success of computational techniques for organic systems has not been duplicated for metal halides. But even when it will be, there remains an important difference. Metal halide molecules are more often than not hot, floppy systems with considerable anharmonicity. These features cannot be neglected and as the very demanding experimental studies are being paralleled by a growing number of computational papers, a critical assessment of experimentally and computationally derived structural parameters and their differences is warranted.

First of all, there is a difference in the physical meaning of computed and experimentally determined structures and this difference can be an order of magnitude larger than the uncertainties of the parameters themselves. Thus, it is an important caveat not to ignore these differences lest we deem our comparisons and conclusions meaningless. A variety of examples will illustrate the severity and the magnitude of this problem. It will also be demonstrated that the critical approach to the wealth of experimental and computational information on these structures is repaid by exciting discoveries of intricacies and the subtleties of metal halide molecular structures, such as the observation of direct evidence of gas-phase Jahn-Teller effect and the structural changes upon molecular association.

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Acknowledgement: The research is being supported by the Hungarian National Research Fund (OTKA T 025788).

GROWTH DYNAMICS OF CARBON NANOTUBES BY LASER ABLATION

S. Iijima
Meijo University, JST/ICORP 'Nanotubulites' Project and NEC R&D Group
34 Miyukigaoka, Tsukuba Ibaraki Japan 305-8501

In-situ observation of the nanotube growth is ideal for understand the nanotube formation. Toward this goal we have utilised two direct methods, shadowgraphy and emission imaging spectroscopy of the laser plume, for studying of growth of graphitic structures which are produced by CO2 laser ablation of graphite. The use of CO2 laser has an advantage over the conventional Nd-YAG laser for longer pulse width and lower laser intensity, which enables us to observe the laser plume over a graphite target in the shadowgraphy technique through a high speed video-recorder. The emission imaging spectroscopy can provide with spatial and temporal distribution of light emission from the laser plume, where the black-body radiation and C2 dimmers emission are predominant. As an example of a CO2 laser ablation product, we introduce SWCNTs with corn-shape caps which aggregates into a spherical particle of ~80nm in diameter. These tubules are formed at room temperature and without metal catalyst, so that the formation is much simpler than that SWCNTs.

K 12

KNUDSEN EFFUSION MASS SPECTROMETRY

J. Drowart

Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium

The basic principles of Knudsen effusion mass spectrometry (KEMS) are summarized and discussed. A broad survey is made of the results and of the incidence of the method in high temperature and in materials chemistry. Recent instrumental developments, applications and results are reviewed.

ION-MOLECULAR EQUILIBRIA IN THE FULLERENES VAPORS

Lev N. Sidorov

Department of Chemistry, Moscow State University, Moscow 119899, Russia

Our results on the gas phase thermochemistry of the higher fullerenes and their derivatives are reported here. We have carried out the direct mass spectrometry measurements of the equilibrium constants of the gas phase ion/molecule reactions involving [70 + 2n] fullerenes (n = 0, 1,...18) and their fluorine derivatives.

INSTRUMENTATION. All experiments were performed in MI-1201 magnetic mass spectrometer modified for measuring both charged and neutral species in high temperature vapors. Nickel effusion cell with the orifice/evaporation area ratio `~ 500 was resistively heated up to 800-1000K. ***Registration of neutral species.*** Electron impact (EI) mass spectrometry conditions were as follows : electron-ionization energy, 70eV, emission current, 0.3-0.5mA and resolution , 840 (10% valley definition). ***Registration of negative ions.*** The negative ions which are in equilibrium with neutral fullerenes species were drawn out of the Knudsen cell and their intensities were measured after passing through the magnetic analyzer. ***Verification of equilibrium.*** In order to prove the reliability of the equilibrium constant measurements of ion-molecular reactions we deliberately changed composition of the samples. For example the partial pressures ratio of C_{70} / C_{60} was veried up to two orders of magnitude due to the sample composition change. It was concluded that equilibrium does exist for electron exchange reactions as well as for fluorine and fluorine anion exchange ones.

HIGHER FULLERENES. Accurate data on the Gibbs energies of the gas-phase anion/fullerene molecule exchange reactions were obtained from the equilibrium constant measurements. The electron affinities (EA) for the series of [70 + 2n] fullerenes (n = 0, 1,...18) were determined. The EA values show an increase with the size of the molecule over the whole range, although disruption from the monotonic change was observed in the series of [70]-, [72]-, [74]- and [76] fullerenes.

FLUORINE DERIVATIVES. Lower fluorinated fullerenes and their anions were generated *in situ* in mass spectrometer by reaction between the highly fluorinated fullerenes with fullerite. From the equilibrium constants for the electron exchange reactions between difluorinated fullerenes and their parents EA's were derived for $C_{60}F_2$ (2.74ev) and $C_{70}F_2$ (2.80). The data on energetics of step-wise fluorine attachment to the fluorine molecules and anions were obtained. One can conclude from these data that the addition of the first F_2 molecule is less exothermic than the succeeding additions to the once fluorinated molecule. It was also established that formation of the molecule with even number of fluorines is more preferable than the odd ones.

ENDOHEDRAL METALLOFULLERENE SOOT STUDY. Both Thermal Ionization (TI) and EI mass -spectra were recorded for the identification of the gas phase composition of the metallofullerene soot samples. Gd and La containing fullerene primary soots were examined. Lager concentrations of the metallofullerene peaks were found in Gd-soot and the species Gd@C_n^- (n=60,74,76,78,80,82) were identified in the TI mass spectra at 810K (Gd@C_{60}) 930K and 960K . The equilibrium constants of electron exchange reactions between C_{60} and Gd@C_{60} and between C_{74} and Gd@Cn (n=74,76,78,80,82) were measured. EA of Gd@C_{60} was estimated as 2.9eV and EAs of Gd@Cn (n=74,76,78,80,82) were estimated as 3.2-3.3eV.

K14

Water Vapor Effects on Silica Forming Ceramics

Elizabeth J. Opila
Cleveland State University/NASA Glenn Research Center
21000 Brookpark Rd.
Cleveland, OH 44135

Silica-forming ceramics (SiC, Si_3N_4, and composites of these) are proposed for applications in many high temperature environments. One such application is for components in combustion environments. Combustion gases contain about ten percent water vapor regardless of fuel-to-air ratio. It is therefore of considerable importance to understand the durability of silicon-based materials, as well as silica, in high temperature water vapor environments.

First, it is well known that the oxidation rate of silica formers is enhanced in water vapor relative to rates observed in dry oxygen. Results from furnace exposures of CVD SiC in H_2O/O_2 at temperatures between 1100 and 1400°C quantitatively establish the dependence of the oxidation rate on the water vapor partial pressure. These results have also been used to show that the predominant mechanism for oxidation in water vapor is by molecular H_2O permeation through the growing silica scale.

Secondly, silica is volatile in water vapor containing environments due to gaseous hydroxide formation by the following reaction:

$$SiO_2 + 2H_2O(g) = Si(OH)_4(g)$$

This volatility has been monitored by weight loss measurements as well as by a specialized atmospheric sampling mass spectrometer. This reaction is shown to have a low temperature dependence. Evidence for formation of other silicon hydroxide species will also be discussed.

Finally, both enhanced oxidation and volatilization occur simultaneously when silicon-based materials are exposed to high temperature water vapor containing environments so that paralinear kinetics are observed. Initially weight gains occur as scale growth dominates the process. At longer times silica scale volatility dominates the process until a steady state is achieved. Linear weight loss and substrate recession rates are then observed. This process has been modeled assuming the volatility is controlled by diffusion of the silicon hydroxide species through a gaseous boundary layer.

Oxidation Mechanisms of Aluminium-Based Intermetallics
- Thermodynamic and Kinetic Aspects -

W.J. Quadakkers, V. Shemet, L. Singheiser
Forschungszentrum Jülich, IWV2
52425 Jülich, FRG

In recent years considerable efforts have been put into research and development of aluminium based intermetallics. These alloys offer the possibility to develop construction materials which combine high temperature strength with low density. Besides, the high aluminium content of the materials offers the possibility to form protective alumina surface scales upon high temperature exposure in aggressive environments.

Most research efforts have been devoted to aluminides of iron, nickel and titanium. Especially the binary compounds FeAl, NiAl and TiAl seem most promising because they possess very high melting points thus offering the principle possibility of very high temperature applications.

From the view point of high temperature oxidation resistance the mentioned iron- and nickel-based intermetallics are generally found to form protective alumina based surface scales even at temperatures as high as 1200°C. The thermodynamic activities of the respective elements in the mentioned binary intermetallic phases are such that under the relevant experimental conditions alumina is the stable oxide in equilibrium with the respective intermetallic compound. Additionally, aluminium diffusion in the compounds is sufficiently fast to form and pertain protective alumina surface scales. The long-term oxidation properties depend on suitable amounts of reactive element additions to improve scale adherence and the distribution of precipitates originating from ternary/quaternary alloying elements added for alloy strengthening.

From the viewpoint of oxidation resistance the most challenging aluminium based intermetallic is γ-TiAl. In this compound the thermodynamic activities of titanium and aluminium are such, that, depending on exact alloy composition, both alumina and titania can be the oxide phases in equilibrium with the alloy. Apart from that, the material possesses considerable solubility for oxygen, thus enhancing the tendency for alumina to form as internal oxide rather than as external, protective scale. The high oxygen solubility is mainly related to the formation of α_2-Ti_3Al in the sub-scale depletion layer. Recent efforts to improve the oxidation resistance of γ-TiAl alloys are based on the following strategies:

- Addition of alloying elements which decrease the amount of lattice defects and consequently the growth rates of the heterogeneous titania/alumina surface scales,
- Addition of alloying elements which suppress the formation of α_2-Ti_3Al in the sub-scale depletion layer thus decreasing the oxygen solubility in the alloy.

K 16

MATERIALS CHEMISTRY & SOFC DEVELOPMENT SELECTED CASE STUDIES

B.C.H.Steele[a], C.B.Alcock[b], A.Atkinson[a]

Fabrication of solid oxide fuel cells (SOFC) usually involves thermal treatments in excess of 1000C. It is essential therefore that the cell components, cathode, electrolyte, anode, substrate, are chemically and structurally compatible during the processing procedures. The strategies adopted to optimise compatibility will be surveyed with comments about recent developments to reduce fabrication temperatures.

Loss of oxygen and the associated lattice expansion under chemical potential gradients can produce significant strains and cause structural failure. This phenomenon can be a problem for $LaCrO_3$ based bi-polar plates, and components based on CeO_2 solid solutions. Relevant data will be summarised to indicate the need for a quantitative model to advance our understanding of these 'chemical expansion' effects.

The volatilisation of chromium from metallic bi-polar plate materials is an important degradation mechanism during SOFC operation. The acquisition of relevant thermo-chemical data has provided explanations for this process as well as suggesting strategies to reduce the degradation rate. The success of these will be briefly examined.

Lower temperature operation (500-700C) is raising questions about the long term stability of oxides in gaseous environments containing CO_2 and SO_2. At the same time there is increasing evidence that at these reduced temperatures the direct electrochemical oxidation of dry methane can yield useful power densities (eg. $0.38Wcm^{-2}$ at 650C[1]). Accordingly the selection of alternative anode materials will provide the final example of how materials chemistry is making important contributions to the development of SOFC technology.

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a). Dept of Materials, Imperial College, London, SW7 2BP (b.steele@ic.ac.uk)
b). Dept. of Materials, University of Toronto, Canada.

Stoichiometry changes and isotope incorporation in single crystal Fe-doped $SrTiO_3$

R. A. De Souza and J. Maier

Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1, D-70569 Stuttgart, Germany.

The kinetics of stoichiometry changes and of isotope incorporation in the model system of Fe-doped $SrTiO_3$ have been studied with the aim of increasing our understanding of oxygen exchange and mass transport in oxide materials. An *in situ* optical absorption technique was employed to examine the kinetics of oxygen stoichiometry changes. Such experiments are based on the fact that, in this system, Fe^{4+} ions act as sensitive, local probes of the degree of oxygen nonstoichiometry. Consequently, by measuring the optical absorbance of Fe^{4+} ions as a function of time and position in the sample during a change in oxygen stoichiometry, the spatially resolved evolution of the oxygen incorporation process can be followed. Analysis of these profiles yields chemical transport coefficients: D_b^δ, for oxygen transport in the oxide bulk, and k_s^δ for oxygen transport across the gas/solid interface.

Oxygen isotope (^{18}O) incorporation was studied by means of *in situ* and *ex situ* techniques. The former consists of monitoring the relative proportions of the various oxygen isotopes in the gas as a function of time by means of a mass spectrometer, and can also provide additional information concerning the mechanism of the surface reaction. The latter involves quenching a sample during an isotope anneal, and subsequently determining the diffusion profile by Secondary Ion Mass Spectrometry (SIMS). Both techniques yield tracer transport coefficients (D_b^*, k_s^*).

In investigating these two different solid state transport processes, experiments were carried out as a function of temperature, oxygen partial pressure and dopant concentration. The results from the two sets of experiments are compared and are interpreted in terms of linear irreversible thermodynamics and kinetic master equations.

Oral Presentations
O1 – O41

O1

High-Temperature In-situ-Detection of Atomic Potassium with NIR-Diode Lasers

E. Schlosser[2], H. Pitz[2], W. Christmann[1], V. Ebert[2]
[1]PreussenElektra Engineering GmbH, Bergmannsglückstr. 41-43, D-45896 Gelsenkirchen
[2]Physikalisch-Chemisches Institut, Universität Heidelberg, INF 253, D-69120 Heidelberg
contact: volker.ebert@urz.uni-heidelberg.de

Since the combustion of fossil fuels –namely coal- will remain an important energy source over the next decades, it becomes an urgent task to minimize CO_2-emission by maximizing the total efficiency of the plant by the use of modern high-temperature combined-cycle combustion processes. However, the high process temperatures lead to an increased release of alkali and heavy metal compounds, which are likely to enhance the corrosion problems in the hot gas turbines. Hence, many turbine producers impose strict limits for these at the entrance of the turbine, and innovative high temperature filters and detailed knowledge of the high temperature chemistry of the alkali compounds is needed. The usefulness of conventional probe sampling techniques to study these systems is in doubt due to the high process temperatures and the high reactivity of the flue gas constituents, so that a direct in-situ detection for the relevant species is required not only for basic physico-chemical research but also to allow on-line monitoring of the high temperature filter function.

For this purpose we developed a compact, diode-laser based absorption spectrometer capable of a highly sensitive in-situ species detection. For a first test we used this device to monitor potassium produced by thermal dissociation of KCl in a high-temperature oven at up to 1000°C. With an absorption length of 6 cm inside the furnace we demonstrated a sensitivity of $7{,}5 \cdot 10^6$ atoms/cm^3. We also determined pressure induced broadening and shift of the absorption line by various collision partners. The first results of an in-situ potassium measurement behind the high temperature filters of an atmospheric coal-combustor will be presented.

O2

OCCLUSION OF MOLTEN CHLORIDE SALTS BY ZEOLITE 4A – NATURE, THERMODYNAMICS, AND APPLICATION TO NUCLEAR WASTE TREATMENT AND DISPOSAL

Dusan Lexa, Leonard Leibowitz, and A. Jeremy Kropf

Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
USA

Glass-zeolite ceramic waste forms are being developed at Argonne National Laboratory for the disposal of radioactive waste salts from electro-metallurgical treatment of spent nuclear fuel. The major component (70 wt%) of the process salt is the LiCl-KCl eutectic salt (58 mol% LiCl, 42 mol% KCl). In addition, the process salt contains NaCl, at least 16 other fission product chloride and iodide salts, and 2 mol% actinide chlorides, such as UCl_3, $NpCl_3$, and $PuCl_3$. The melting temperature of the process salt is ~ 600 K. Two options are being explored for the process salt treatment:

- Batch method. The process salt is blended with dehydrated zeolite 4A granules (10 wt% salt, 90 wt% zeolite) at ~ 823 K, producing an occlusion compound with the salt residing inside the zeolite 4A cages. The salt-loaded zeolite is combined with glass (75 wt% zeolite, 25 wt% glass) and HIP-ed.
- Column method. The process salt is passed through a column charged with LiCl-KCl pre-loaded zeolite 4A beads at ~ 823 K. The effluent salt, ideally LiCl-KCl, is re-used. The salt-loaded zeolite, enriched in fission product and actinide chlorides, is ground, and processed as above.

As a first step in understanding the interaction between the salt and the zeolite, the occlusion of the LiCl-KCl eutectic salt by zeolite 4A have been studied by *in situ* temperature-resolved synchrotron powder X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Because of indications of possible reaction between UCl_3 and zeolite, the occlusion of the UCl_3-LiCl-KCl eutectic salt by zeolite 4A have been studied by *in situ* temperature-resolved synchrotron powder X-ray diffraction (XRD), evolved gas analysis, and differential scanning calorimetry (DSC). Equilibrium ion-exchange zeolite 4A / molten salt separation factors have been determined in a number of pseudo-ternary systems, including NaCl-LiCl-KCl, CsCl-LiCl-KCl, $SrCl_2$-LiCl-KCl, $BaCl_2$-LiCl-KCl, $LaCl_3$-LiCl-KCl, and $CeCl_3$-LiCl-KCl, by chemical analysis of both the zeolite and the molten salt phases.

The Intermetallic Compound Ni_3Ga: Nonstoichiometry and Thermodynamics

Wenxia Yuan, Hans Ch. Flandorfer, and Herbert Ipser
Institut für Anorganische Chemie, Universität Wien, Währingerstr. 42, A-1090 Wien, Austria

The intermetallic compound Ni_3Ga crystallizes in the cubic $L1_2$-structure like the isostructural Ni_3Al-phase. Although Ni_3Ga might exhibit similarly interesting properties as the latter compound, not much seems to be known about its properties which is certainly caused by the much higher cost of metallic gallium; nevertheless, Ni_3Ga might still be of interest for some specific applications.

Experimental thermodynamic activities of gallium in Ni_3Ga were determined as a function of temperature and composition by an emf-method using yttria-stabilized zirconia as solid electrolyte. From these measurements all partial thermodynamic properties of gallium were derived over the entire composition range. A statistical-thermodynamic model was applied to the activity data to derive the defect mechanism that is responsible for the deviation from stoichiometry. It was found that anti-structure atoms (substitutional defects) are the main types of defects present whereas vacancies seem to play a negligible role. The energies of formation of the various types of defects were estimated by comparing the experimental activity data with the model curves.

Solution calorimetry in liquid gallium was performed to determine the enthalpy of formation, $\Delta_f H$, in the Ni_3Ga-phase as a function of composition. Furthermore, a high temperature calorimeter was used to determine the heat capacity, Cp, of various Ni_3Ga alloys. All experimental data will allow a full description of the thermodynamics of Ni_3Ga and will be available for an optimization of the binary Ni-Ga system.

O4

Enthalpy of formation and description of defect structure of the intermetallic compound B2-FeAl

J. Breuer, F. Sommer and E.J. Mittemeijer

Max Planck Institute for Metals Research
Seestrasse 92, D-70174 Stuttgart, Germany

Many ordered intermetallic compounds are homogeneous over a wide range of composition near stoichiometry. The defect structure of those alloys is strongly influenced even by small deviations from stoichiometry. Excess atoms of one species have to be compensated by structural vacancies and/or antisite atoms. Additional defects caused by thermal activation exist. Types and concentrations of defects have great impact on the mechanical properties of intermetallics promoting numerous experimental and theoretical investigations on this topic.

B2 (or CsCl) structured intermetallic compounds are traditionally divided into two groups depending on their defect structure: the so-called anti-structure type and the triple-defect type. Whereas for B2-NiAl and B2-CoAl the triple-defect structure is compatible with the experimental data (compounds with a surplus of Al contain vacancies in the Ni-/Co- sublattice, and antisite atoms in the Al- sublattive compensate for a surplus of Ni or Co.), this is not true for B2-FeAl.

In order to obtain thermodynamic access to the defect structure of the ordered B2-phase FeAl, the heat of formation was experimentally determined by solution calorimetry at $T = 1073\,K$ as a function of composition in the range 30 to 50 at% Al. The enthalpy of formation of FeAl is negative, $-36.2\,kJmol^{-1}$ at the equiatomic composition. The absolute value of the enthalpy of formation decreases with increasing deviation of the composition from stoichiometry. In contrast with B2-NiAl and B2-CoAl, that show a clear linear decrease of the absolute enthalpy values with increasing deviation from stoichiometry, for B2-FeAl a non-linear behaviour was found.

Applying statistical thermodynamics the enthalpy of formation is described over the whole composition range of B2-FeAl. The results show that B2-FeAl exhibits a rather complicated defect structure where more than one type of defect per sublattice occurs.

Al-Sn-Zn Alloys
A new Lead-free solder material?

S. Knott and A. Mikula

Institut für Anorganische Chemie
Währingerstraße 42, A-1090 Vienna, Austria

Unique physical and mechanical properties made the Pb-Sn solders attractive for low temperature joining of electronic parts. This type of solder materials has been used extensively in the electronic industry as a primary method for interconnecting electronic components. Since lead is considered to be toxic, these solder joints became a great environmental problem and health concern in electronic waste management. Electronic companies responded by starting intensive research for new lead-free solder materials.

The most important property for an alternative material is the melting temperature. The temperature can not be too high, because this might damage the components which should be joined together and could also induce thermal defects in the electronic parts. The temperature should also not be too low, the typical electronic equipment in cars must operate between $-50^{o}C$ and $+175^{o}C$.

Looking through the phase diagrams in the literature there are only a few binary tin systems which would be suitable for solder materials in this temperature range. Tin based alloys are chosen because tin reacts with a wide range of metals to form stable connections and has also a good wettability for many substrates. Therefore it is necessary to focus the research on multicomponent systems.

On the Al-Sn-Zn system the microstructure, wettability and oxidation resistance were investigated by Lin and coworkers[1,2] and we determined the thermodynamic properties of the liquid alloys over the whole composition range with an emf method and measured the liquidus temperatures with DTA. The results will be presented at the conference.

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O6

Molten Rare Earth Halides: Structure and Thermodynamics

G. N. Papatheodorou

Institute of Chemical Engineering and High Temperature Chemical Processes
P.O. Box 1414, GR-265 00 Patras, Greece

Raman spectroscopy has been used to study the structural properties of molten trivalent rare earth halide RX_3 (R=La, Nd, Gd, Dy, Ho, Y, Sc; X=Cl, Br) and their mixtures with alkali halides RX_3-AX (A=Li...Cs). In mixtures rich in AX the predominant species are the RX_6^{3-} octahedra. With increasing RX_3 content the spectra for all sets of binaries studied are characterized by two polarized and two depolarized bands. The frequency and intensity variation of these bands with mole fraction suggest that the melt structure consists of RX_6^{3-} octahedra bound by edges. It also appears that the structure of all RX_3 melts are similar and independent of the structure of the corresponding solid. The systematics of the vibrational frequencies of the RX_6^{3-} octahedra are correlated to the few available enthalpy of mixing data of the corresponding binary mixtures RX_3-AX. Based on this correlation the enthalpies of mixing of unknown binary melts can be estimated.

O7

Thermodynamic Properties of $Ce_{1-y}Hf_yO_2$ (y=0 – 0.30)

Toshihide TSUJI*, Hiromasa MITANI** and Yasuhisa YAMAMURA*
*Center for New Materials, Japan Advanced Institute of Science and Technology, Hokuriku, 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292 Japan
**Department of Nuclear Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

Thermodynamic properties of ZrO_2, HfO_2 and CeO_2 doped with lower valent cations have been studied from the viewpoints of solid electrolyte fuel cell by many investigators. However, studies on thermodynamic properties of these mixed oxides with the same valence, (Ce, Hf)O_2, are lacking. In this paper, thermodynamic properties such as linear thermal expansion (LTE), solubility limit and heat capacity for $Ce_{1-y}Hf_yO_2$ were studied by low- and high-temperature X-ray diffractometry and thermodilatometry.

Analytical reagent grade CeO_2 and HfO_2 powders of the required proportion were mixed in an agate mortar, pressed into a cylindrical pellet and then sintered for 40 h at 1773 K in air. Low- and high-temperature X-ray diffraction measurements of $Ce_{1-y}Hf_yO_2$ (y=0–0.30) were carried out at temperatures 123-473 K in vacuum and 300-1273 K in air, respectively by Rigaku RINT 2500V X-ray diffractometer. The LTE values were measured from 90 to 1673 K by thermodilatometry.

The lattice parameters of $Ce_{1-y}Hf_yO_2$ (y=0–0.10) increased smoothly with increasing temperature from 123 to 1200 K, indicating that no phase transition occurs in the temperature range investigated. Measured lattice parameters were fitted as function of temperatures in the form of $a_T = b_0 + b_1T + b_2T^2 + b_3T^3$ where a_T was the lattice parameter at temperature T(K). The LTE of $Ce_{1-y}Hf_yO_2$ (y=0–0.10) decreased with increasing y value. However, the LTE values of CeO_2 in this study were larger than those by TPRC above 1200 K, probably due to defect formation at higher temperatures. The lattice parameters at each temperature increased linearly with increasing the y value, reflecting the Vegard's law, and a rigid sphere model could explain the slope. The specific heat capacities at constant pressure C_p of these solid solutions were calculated from the thermodynamic relation $C_p(JK^{-1}mol^{-1}) = \beta V/\kappa_s \gamma$ using the measured thermal expansion data and estimated mechanical properties. The calculated C_p curves showed similar temperature dependence to the literature ones.

The solubility limit of y in $Ce_{1-y}Hf_yO_2$ (y=0–0.30) was determined to be y=0.18 from change of the slope in the plots of lattice constants against the y value.

O8

DESCRIPTION OF THE QUATERNARY SYSTEM Bi/Te/Se/O AND THERMODYNAMIC MODELING OF THE PHASE DIAGRAMS

Peer Schmidt, H. Oppermann
Institut für Anorganische Chemie
der Technischen Universität Dresden

The phase relations in the quaternary system Bi/Te/Se/O have been studied for the ternary and pseudoternary areas Bi/Te/O [1 - 3], Bi/Se/O [4 - 6], Te/Se/O [7], $Bi_2O_3/TeO_2/SeO_2$ [7] and $Bi_2O_3/Bi_2Te_3/Bi_2Se_3$ [8] by solid state reactions and chemical transport. For the pseudobinary systems we determined the thermochemical behaviour by x-ray, total pressure measurements and thermal analysis and concluded the phase diagrams. The composition of the gaseous phase have been determined by mass-spectrometry.

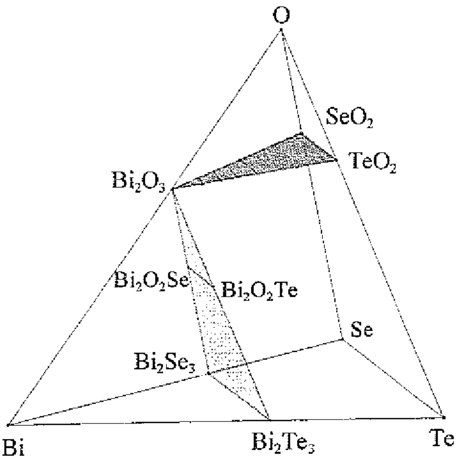

Fig. 1 The quaternary system Bi/Te/Se/O

We demonstrate in the particular case of the systems Bi/Te/O and $Bi_2O_3/Bi_2Te_3/Bi_2Se_3$ the determination of the thermodynamic data of compounds and solid solutions $Bi_2(Te_xSe_{1-x})_3$ and $Bi_2O_2(Te_xSe_{1-x})$. In which result we can completly thermodynamicaly describe the observed phase relations in the (pseudo-) ternary areas by modeling of the equilibria of solid state - gaseous phase [P1].

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NITROGEN CERAMIC MATRIALS PREPARED USING COMBUSTION (SHS) METHOD

Jerzy Lis

Department of Advanced Ceramics, Faculty of Materials Science and Ceramics
University of Mining and Metallurgy - AGH
Al. Mickiewicza 30, 30-059 Kraków, Poland
lis@uci.agh.edu.pl

The combustion method, called Self˜Propagating High˜Temperature Synthesis (SHS), can be used as a source of highly sinterable multi-phase ceramic powders. Such the powder precursors are useful for preparation of ceramic materials having attractive properties. The paper presents results of author,s investigations on nitrogen ceramics in the system Si-Al-O-N prepared using SHS-derived powders. Because of specific mechanisms occurring during rapid, combustion-type SHS reactions the nitride powders prepared by the SHS method can been obtained in a specific no-equilibrium state. Followed high-temperature densification has a reactive sintering character, joining in a complex form the densification phenomena with chemical reactions, phase transformation phenomena, grain grown processes, etc. It makes possible to multidirectional control of materials microstructure evolution during sintering and obtain desirable properties in final materials. The SHS-synthesis in the Si-Al-O-N system has been focused on preparation of the powders having different chemical and phase composition in a metastable equilibrium. A preparation of the powders by the combustion, sintering phenomena and materials evaluations are reported with perspectives of an application of such materials as a structure ceramics are discussed in details.

O10

HT-Mechanical Properties of Si-B-C-N Precursor-Derived Ceramics

G. Thurn, M. Christ, A. Bauer, J. Bill, and F. Aldinger

Max-Planck-Institut für Metallforschung

and

Universität Stuttgart, Institut für Nichtmetallische Anorganische Materialien,

Pulvermetallurgisches Laboratorium, Heisenbergstrasse 5, 70569 Stuttgart, Germany

Amorphous Si-B-C-N ceramics have been fabricated by thermolysis of organometallic polymers. The polymers were crosslinked at different temperatures. After milling and sieving an infusible polymer powder was obtained. The powder was densified under uniaxial compression stress in the temperature range between 150°C and 300°C where the polymer can be deformed plastically. The influence of the processing conditions on the porosity and the mechanical properties of the ceramic, obtained after thermolysis at 1400°C was investigated. The Compression creep behavior of these ceramics was measured at temperatures up to 1550°C and stresses up to 300 MPa. Within the testing time of up to 500 hours, the strain rate decreased several orders of magnitude and stationary creep was not observed. A reduction of strain rate during the creep test is accompanied by a reduction of free volume in the amorphous matrix. Solid state NMR-MAS investigations were carried out to investigate structural changes of the amorphous matrix during the creep tests. It can be shown that the strain rate consists of a component with linear dependence on the creep stress, and a component independent on the applied stress. Diffusion are viscous flow are thought to be the major creep mechanisms. The creep resistance of the ceramics can be improved by temperature and/or pressure treatments after thermolysis.

Synthesis of Titanium Carbide by Reaction of Titania with Methane-Hydrogen Gas

Guangqing Zhang, Oleg Ostrovski
School of Materials Science and Engineering, University of New South Wales, Sydney 2052, Australia. Tel. +61-2-9385 4439 Fax +61-2-9385 5956 Email O.Ostrovski@unsw.edu.au

Synthesis of titanium carbide by reaction of titania with methane-hydrogen gas was investigated in a laboratory fixed bed reactor. The reaction product is titanium oxycarbide, which is a solid solution of TiC and TiO. A sequence of titania reduction to titanium oxycarbide is as follows:

$$TiO_2 \longrightarrow Ti_5O_9 \longrightarrow Ti_4O_7 \longrightarrow Ti_3O_5 \longrightarrow Ti_2O_3 \longrightarrow TiO_xC_y$$

The effect of temperature on the titanium carbide synthesis was examined in the range 1373-1773 K. At 1373 K the formation rate of TiC is very slow. The rate and extent of reaction increase with increasing temperature to 1723 K. Further increase in temperature to 1773 K does not affect the reaction rate. At 1673-1773 K, extent of reduction of titania to titanium oxycarbide, defined as percentage of oxygen removed, achieves more than 85% in about 90 min. This means that the TiO-TiC solid solution contains about 70 wt% of TiC.

The reduction and carburization rates increase with increasing methane content in the CH_4-H_2-Ar gas mixture to 8 vol%. Further increase in the methane concentration causes excessive methane cracking with solid carbon deposition, which hinders access of the reducing gas and decreases carbon activity in the system. An increase in temperature above 1723 K has a similar effect. To depress the deposition of solid carbon concentration of hydrogen in the gas mixture should be above 35 vol% (at 1573 K and 5 vol% CH_4).

Addition of water vapor to the reducing gas retards strongly the reduction reaction even at low concentrations of 1-2 vol%. Carbon monoxide also depresses the reduction process but its effect is significant only at higher concentrations, above 10 vol%.

Optimum conditions for titanium carbide synthesis from titania and methane-hydrogen-argon gas mixture include temperature in the range 1573-1723 K, methane content of 8 vol% and hydrogen content above 35 vol%.

O 12

Microstructural Development and Phase Stability of Mo_{ss} - Mo_5SiB_2 *in-situ* Composites

G. Wilde[1,2], R. Sakidja[1], Z. Dong[1] and J. H. Perepezko[1]

[1] University of Wisconsin-Madison, Department of Materials Science and Engineering, Madison, WI 53706, USA

[2] Forschungszentrum Karlsruhe GmbH, Institut für Nanotechnologie (INT), D-76334 Eggenstein Leopoldshafen, Germany

Mo_{ss}-Mo_5SiB_2 two-phase alloys are candidate materials for a new class of structural materials that offer a higher temperature limit for applications than conventional high-temperature materials. In the present study, ternary alloys in the composition range of the two-phase field between the Mo solid solution (Mo_{ss}) and the ternary intermetallic compound Mo_5SiB_2 (T2) have been produced by employing different solidification methods and subsequent annealing. In order to revise and establish the equilibrium phase boundaries within that composition area, thermal analysis, transmission electron microscopy and metallographic techniques were employed.

As a next step, the range of microstructural modifications available by solidification processing has been sampled for selected compositions by cooling rate variations that yield different levels of metastability during the solidification reaction. Conventionally arc-melted alloys on one hand reveal microstructures with large compositional segregation including the formation of additional phases. Consequently, extensive annealing at high temperatures is required for prolonged times to obtain the equilibrated Mo_{ss}-T2 alloys. The use of Rapid Solidification Processing (RSP) techniques on the other hand yields the two-phase alloys on a fine scale directly from the melt, as indicated by TEM investigations. Moreover, the results of high-temperature annealing treatments indicate that the two phases are stable on a micrometer scale even after annealing for 150 h at temperatures as high as 1600 °C. The key parameters of the processing pathway that leads to these novel microstructures will be discussed to provide a better understanding of the alloy design and the processing conditions of this high-temperature structural material. The support of the Alexander von Humboldt-Foundation via the Feodor-Lynen-Program (V-3-FLF-1052606) and AFOSR (F 49620-96-1-0286) is gratefully acknowledged.

Concepts for high temperature materials based on oxidic composites reinforced with single crystalline fibres

Dieter Sporn, Reinhard Krüger and Gerd Müller

Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, D-97082 Würzburg, Germany

Silicon based covalently bonded ceramic materials exhibit natural limits in terms of their thermal stability at high temperatures above 1500°C in oxidising atmospheres. This is due to the thermodynamic stability of the oxidation products, e.g. silica. Therefore, it is obvious that oxidic ceramics are more suitable candidates to be applied at such temperatures, especially for long term applications. Caused by the comparably lower bonding energy oxidic ceramics have their own limits: they creep distinctly faster in comparison to nonoxidic ceramics. This problem may be solved by reinforcing components, like fibres. The commmercialised oxidic fibre types are polycrystalline, but they do not survive temperatures above 1300°C. Available single crystalline fibres exhibit high strength and Young's modulus values as well as creep resistance, even at high temperatures, but large diameters (> 100 (m). These dimensions and the high price values are hindering reasons for the development of composites.

A conceptional material with oxidic matrix and reinforced with thin, single crystalline oxidic fibres will be discussed in terms of choice of the suitable material systems (matrices, fibres and interfaces). The main focus will be on alternative routes to produce single crystalline oxidic fibres with diameters smaller than 30 (m. In the near future this process will allow the fabrication of fibres in multifilament approach.

O14

Ternary Phases in the System Al/B/C

Falko D. Meyer and Harald Hillebrecht
Universität Bayreuth, Lehrstuhl ACI, Universitätsstr. 30, 95447 Bayreuth, Germany

Composite materials made of an aluminium based matrix reinforced with boron carbide fibres are promising candidates for aerospace applications. In view of optimizing the production of such materials by melt infiltration, a general study of the reactivity of liquid aluminium towards boron carbide has been undertaken.

The aim of the investigation was the synthesis of pure compounds in the system Al/B/C and their characterisation.

The compounds were synthesized in molten aluminium, by solid-state reaction and by high-temperature synthesis. The preparative work was done in a high-temperature furnace with graphite heater.

The phases were characterized by the means of X-ray single crystal structure analysis, X-ray powder diffraction, FT-IR- and FT-Raman-spectroscopy, UV/Vis and DTA measurements. Quantitive analyses was done by WDX and RBS measurements.

The crystal structures of the boron-rich borides B48Al3C2 and B51Al2C8 are based on B12-icosahedra. B48Al3C2 is close related to the so called "tetragonal boron I". It is possible to substitute aluminium partly by silicon, copper, titanium, and vanadium.

B51Al2C8 could be described as modified variant of boron carbide.

The crystal chemistry of Al3BC and Al3BC3 is related to that of aluminium carbide, Al4C3. By the means of vibrational spectroscopy and structure analysis, isolated CBC5- anions could be determined in Al3BC3. Because of its relativly low melting point, the formation of Al3BC3 seems to be responsible for the supporting character of Al additions by sintering boron carbide at high temperatures.

Al3BC is built at low temperatures from boron carbide and aluminium.

Al4C3 shows a high solubility for boron. Up to ca. 20% of the carbon atoms can be substituted by boron leading to a change in colour (from yellow to red) and an increase of the chemical stability against hydrolysis. By substitution of carbon by boron, Al4C3 becomes a semiconductor.

O15

Silicon Carbide Synthesis from Rice Husk: Effect of Chemical and Hydrothermal Treatments

K.Sujirote, P.Thavorniti, P.Saewong, and T. Pothsree
National Metal and Materials Technology Center,
NSTDA building, Rama VI Road, Bangkok 10400 THAILAND

The potential and limits of rice husk to become a competitive source of homogeneous, micron-sized silicon carbide were investigated. Husk samples were submitted to chemical and/or hydrothermal pretreatment using Fe_2O_3 or NH_4OH solution. Parts of the samples were pyrolysed at 1000°C under static and flowing inert atmosphere to produce charred husk. Subsequently, all samples were pyrolysed in argon at 1350-1500°C. The converted rice husks were characterised in terms of silicon carbide phase content and morphology, carbon residue, particle size distribution, and specific surface area (BET, N_2). The present study has revealed that though raw rice husk can react in inert atmosphere to form fine SiC whiskers and particulates, both hydrothermal and chemical treatments act as catalyst in increasing the formation of SiC. In addition, carbon in the raw husk reacts more completely than those in the charred husk. The rearrangement of carbon chains, as characterised by solid-state NMR technique, is a key factor that controls the SiC formation. Optimum process conditions were considered for economy of large scale production.

O 16

Thermochemical Modeling of Glass: Application to High-Level Nuclear Waste Glass

Karl E. Spear, Theodore M. Besmann*, and Edward C. Beahm**

Materials Science and Engineering, 118 Steidle Building, Pennsylvania State University,
University Park PA 16802
*Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
**Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Predictive thermochemical models for complex oxide glass systems will not only facilitate technological advances in the glass industry, but they will be especially important for ensuring the environmental integrity of glasses to be used in the disposal of high-level nuclear wastes (HLW). This paper discusses our attempts to develop an accurate, easy to understand and use glass solution model for describing the thermodynamic stability of complex oxide glasses. With such a model, predictions can be made on the stability of nuclear waste forms, including their volatility, leaching behavior, corrosion reactions, and the tendency for crystallization during both the initial glass processing and long-term storage.

Since alkali borosilicate glasses have been chosen as a typical base composition for storing HLW, we initiated our modeling efforts on the Na_2O-Al_2O_3-B_2O_3-SiO_2 system and all of its subsystems. Critical for such a model is reliable thermodynamic data that can be used in generating accurate values for thermodynamic activities of glass components as a function of temperature and glass composition. Therefore, a major part of this paper focuses on developing reliable sets of thermodynamic data for complex HLW glass systems and subsystems. Our model treats the glass as a supercooled liquid, and we use liquid associate species to representation the glass solution phase. Stable and metastable immiscibility in the glass systems is modeled using positive regular solution constants for interactions between liquid associate species. In developing the thermodynamic datafile for the quaternary Na_2O-Al_2O_3-B_2O_3-SiO_2 system, the thermodynamic and phase diagram data for the six binary and four ternary subsystems were assessed. The primary process used in the data assessment and estimation involved comparing computed and published binary and ternary phase diagrams, with adjustments in data made as necessary to obtain consistent thermodynamic values. One of the initial applications of these assessed data has been to help understand the problem of nepheline ($NaAlSiO_4$) precipitation in certain waste glass formulations.

Support by DOE under contract DE-AC05-96OR22464 with Lockheed
Martin Energy Research Corporation is gratefully acknowledged.

Application of thermodynamic databases to the simulation of microstructure coarsening in steels

Andrei Prikhodovski, Iñaki Hurtado, Dieter Neuschütz

Lehrstuhl für Theoretische Hüttenkunde, RWTH Aachen,

D-52056 Aachen, Germany

Modelling has proven to be an efficient way of cutting time and costs associated with the investigation of material properties. In this paper the model of diffusional coarsening in multicomponent systems is described. This model is a further elaboration of the mean-field statistical formalism of coarsening analysis first provided by Lifshitz, Slyozov and Wagner (LSW theory). Contrary to the majority of existing descriptions, where an asymptotic analysis of the problem is explored, the accent in the present work is made on the numerical solution of the continuity equation of the particle size distribution (PSD) function. The CALPHAD-type thermochemical data has been used for the equilibrium computations and calculation of chemical diffusion coefficients. The influence of non-zero volume fraction of secondary phase has been also considered.

The present model has been applied to the simulation of the precipitation coarsening in high-strength low-alloyed steels, where the size and spatial distribution of particles are of crucial importance for the mechanical properties of the material. The evolution of the PSD function has been obtained and compared with the experimental observations available in the literature. Another application of the model is the simulation of the coarsening in steel subject to semi-solid material processing (thixoforming), where steel billets are preheated and held isothermally at temperatures within the solidus-liquidus range. In order to achieve optimum processing conditions a required liquid fraction is to be set, while at the same time microstructural coarsening is to be minimised.

O 18

Modelling of the LD-Converter-Process with focus on non-equilibrium phenomena

Prof. Dr.-Ing. M. Modigell, Dipl.-Ing. A. Traebert, Institut für Verfahrenstechnik, RWTH Aachen, Turmstr. 46, 52056 Aachen, Tel: 0241-805484, Fax: 0241-8888-252,
email: traebert@ivt.rwth-aachen.de;
Dr. P. Monheim, Mannesmann Demag Metallurgie, Dept. 6278, Wolfgang-Reuter-Platz,
47053 Duisburg

Due to high reaction rates and high mass and heat transfer rates in turbulent flow, high-temperature processes usually show a behaviour close to thermochemical equilibrium. A detailed analysis of metallurgical processes shows that reacting components are often distributed on multiple phases, which are not in equilibrium. These deviations from equilibrium are caused by considerably limited heat and mass transfer, e.g. due to incomplete mixing. A modelling technique was developed to enable the calculation of such complex non-equilibrium phenomena. With this technique, a process is simulated using an appropriate arrangement of simple, local equilibrium reactors coupled by defined heat and mass transfer. Heat and mass transfer is calculated from process boundary conditions.

The simulation of a LD Converter Process was undertaken applying this technique, with a focus on non-equilibrium phenomena. In modelling great stress was placed on a state of the art representation of the thermochemistry of the material systems involved. A newly developed modular process balancing system was successfully applied incorporating the thermochemical applications library ChemApp^{R}, which is well known for its abilities to treat the chemistry of metallurgical processes.

The validation of the simulation model shows good agreement between reported and calculated values for species concentration and temperature development in time. Real-process phenomena can be predicted. It is intended to extend the current research to cover other metallurgical processes with the aim to obtain a tool not only for the design and simulation of established processes, but also for the development of new process routes. The potential of such process modells for process control is discussed.

Thermodynamic assessment of the oxide phases in the Fe-Zn-O system – Application to dust formation in electric arc furnace

Philippe ROCABOIS[1], Jean-Christophe HUBER[2], Eric LECTARD[1], Fabrice PATISSON[2]

[1] IRSID - Groupe Usinor, Voie Romaine BP 30320 - 57283 Maizières-lès-Metz Cedex, France

[2] LSG2M, Ecole des Mines de Nancy - Parc de Saurupt - 54042 Nancy Cedex, France

Steel production by melting zinc-coated iron scrap in Electric Arc Furnace (EAF) co-produces 15 to 20 kg of dust per ton of steel. This dust is made of metal oxides and mainly contains iron and zinc. Steelmakers are switching from a waste disposal solution to a co-product recycling strategy. To be environmentally and economically sound, this approach requires an increase in the recoverable part of dust to reach a quality level which fits the specifications for zincmaking units (Waelz furnaces, Imperial Smelting furnaces or hydrometallurgical vessels like Rezeda).

Zinc oxide in EAF dust is present in two phases: zincite (ZnO) which is easily recoverable by hydrometallurgy or by pyrometallurgy and a spinel phase $(Fe,Zn)Fe_2O_4$ which results in secondary waste. To suggest some appropriate operating conditions in EAF, i.e., increasing ZnO part against spinel, the mechanisms of dust formation must be well understood. Therefore, the thermodynamic properties and relationships of phases in the Fe-Zn-O system have been assessed with available experimental data : ternary phase diagram and activity measurements of oxygen in various solid solutions[1,2]. The critical binary Fe-O system is described with an associated solution model[3]. The same model has been applied to the modelling of wustite containing ZnO, zincite containing $Fe_{1-x}O$ and the liquid phases. A three sublattice model is applied to the spinel phase. Parameters of all these solutions have been evaluated to reach consistency with experimental data.

The obtained data file was used to calculate the stability domains in a P_{CO_2}/P_{CO} versus temperature diagram for different Fe/Zn ratios. Measured operating conditions of an industrial furnace (fume extraction system) and dust analysis (XRD, SEM) are compared with calculated results. It is found that oxidising conditions lead to a Zn-rich spinel phase to the detriment of the valuable ZnO phase.

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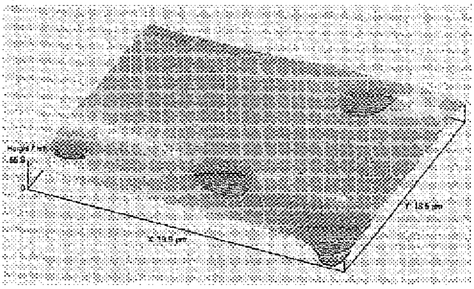
O 20

CORROSION OF SILICA AND HARD GLASS LAMP ENVELOPE MATERIALS BY HIGH TEMPERATURE LAMP ATMOSPHERES

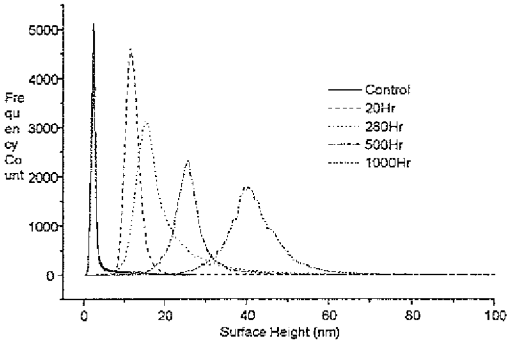
R. Devonshire, J.C. McGourlay and R.J. Forrest
High Temperature Science Laboratories, Chemistry Department,
University of Sheffield, Sheffield, S3 7HF, UK. E-mail: r.devonshire@sheffield.ac.uk

This paper will present an overview of our most recent studies of the corrosion of lamp envelopes during lamp operation. A wide range of surface and vapour phase diagnostics are being exploited to unravel qualitative and quantitative aspects of these complex phenomena which occur both in the aggressive atmospheres of high pressure discharge lamps and in the more benign conditions found in halogen incandescent lamps.

The methodology involves analysis both of lamp envelopes following lamp operation and of ampoules constructed from the same grade materials and "operated" in a temperature gradient furnace. The surface diagnostic techniques being used are SPM (in particular AFM), EDS, SEM, TDS-MS and Laser Ablation ICP-MS, all of which involve breaking the envelopes/ampoules to obtain fragments for examination. These studies are supplemented by high sensitivity, microscopic scale non-destructive spectroscopic techniques able to detect Si containing vapour phase species implicated in SiO_2 transport and to identify substances active at the vapour-glass interface.



The adjacent Figure shows an AFM image of an area 19.9 μm x 16.5 μm from the interior surface of a wall fragment from an operated metal halide lamp. In this image the pits extend to a depth of 55 nm below the surface plane. Image analysis of the pit size and spatial distributions in large area AFM images as a function of "operating" time provides pseudo-kinetic data for materials transport for a given combination of envelope material, dose, temperature profile and operating position. Such data supports quantitative comparisons of the factors influencing corrosion rates.



The AFM derived results in the second Figure show the evolution of inner wall surface height distributions of a hard glass halogen incandescent lamp design as a function of lamp operating time. The systematic development of features of the wall's morphology with operating time nicely illustrates the ability of surface diagnostic techniques to provide quantitative measures of corrosion even for moderate lamp chemistries.

The application of a diverse range of diagnostic techniques is enabling us to create a comprehensive picture of both hard glass and silica lamp envelope corrosion phenomena.

O21

Reliability in ceramic metal halide lamp design

C. L. Ning, C. Scott*

GE Lighting, Melton Road, Leicester LE4 7PD, UK
*GE Lighting, Nela Park, Cleveland, Ohio, USA

Ceramic metal halide (cmh) is a new type of high intensity discharge lamp. Comparing with the conventional quartz metal halide cmh offers much better colour consistency and colour rendering index, higher efficacy and better lumen maintenance, better dimension/volume control and longer life. Since the launch it has been widely used in retail, sports, public and other lighting applications.

The superb performance of cmh lamps comes from its ceramic discharge vessel that is resistant to sodium loss at high operating temperature. It is well known that in quartz metal halide the sodium from the dose can migrate through the quartz wall during operation of the lamp. This sodium loss results in changes of the colour of the lamp. The leaked sodium also blackens the discharge vessel and outer jacket, thus reducing the lumen output of the lamp and the useful lamp life.

To overcome the sodium loss problem in the quartz metal halide a discharge vessel made of polycrystalline alumina (PCA) was developed as alumina is well known to be resistant to sodium attack at high temperature. Obviously to sustain the discharge at high pressure and temperature the ceramic vessel must be hermetically sealed. A conventional cmh arc tube is made by sintering 5 pre-sintered parts together. The pre-sintered parts are made by extrusion. The advantage of this design is that all the parts can be made by extrusion which is a simple and cheap manufacturing process.

The 5-part arc tube has four hermetic PCA-PCA seals. Each seal has a potential to fail during production and lamp life since the arc tube operates at well above 1000C and 10-atmosphere pressure with a very corrosive dose pool inside. The highly corrosive environment inside the arc tube requires long lasting high quality seals and seal integrity. To make a high quality seal the surface of the joining parts must be perfect and free of any distortion in shape. In the extrusion, long tubing is made and then cut into the suitable length in the pre-sintered state. During cutting and following processes defects and distortion can be produced. These defects and distortion will produce poor seals in the sintered arc tube, including micro cracks and micro channels. Arc tubes with these defects would fail in early life of the lamp.

As at each seal there is a possible weak point, to reduce the number of seals in the arc tube should increase the reliability of the arc tube. To reduce the number of seals a 3-part design was considered and tested. In this design, the leg and plug are made of one piece by injection moulding of ceramic powder. Fig.1 In the 3-part design the arc tube has only 2 co-sintered seals. Since the injection-moulding produces exact pre-sintered part dimensions it also eliminates the process of cutting and polishing used in making the extruded leg and plug. This also reduces the defects and distortion in the pre-sintered parts and thus the defective seals in the final arc tube.

The new design has been tested in a commercial environment and has shown significant improvement in both the reliability of the CMH lamp and manufacturing efficiency.

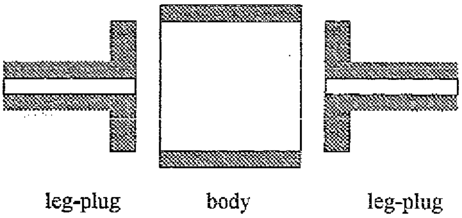


Fig.1 3-part cmh assembly

O22

Characterization of translucent polycrystalline alumina in lamps

G.C. Wei
OSRAM SYLVANIA INC.
71 Cherry Hill Drive
Beverly, MA 01915
USA

Translucent polycrystalline alumina (PCA) serves as housing for high-temperature corrosive plasma in high-pressure sodium and metal halide lamps. Transmittance and sodium resistance are two important properties of PCA related to its microstructure including grain size, second phases, residual pores, grain boundary segregation, and impurities. This paper will focus on the mechanisms of (1) sintering, and (2) sodium resistance of PCA. The relationship between the microstructure, properties, and performance, will be presented. Sintering of alumina doped with magnesia-based additives to translucency was achieved in N_2-H_2 atmospheres containing as low as 2% hydrogen. Experiments on varying the H_2 content and water vapor content of the sintering atmosphere, and dynamic atmosphere changes were conducted. The evidence indicated that the final-stage sintering involved a point-defect pair mechanism including hydrogen interstitials and nitrogen solutes. Reaction of sodium with polycrystalline alumina (PCA) arc tubes in high-pressure sodium lamps can limit lamp performance. The rate of degradation depends on the grain boundary diffusion of a reaction product, Al, through the PCA wall. Key material parameters for sodium resistance were the spinel ($MgO{\bullet}Al_2O_3$) second phase and grain boundary MgO level. Eliminating spinel in the sintered body, doping with tetravalent cations to charge-compensate the Mg^{+2} solutes, and/or creating a second phase to absorb MgO in-situ, significantly improved the resistance of PCA to sodium attack.

High-Temperature Chemical Reactivity Studies Under Concentrated Solar Radiation

M. Sturzenegger, Th. Frey, E. Steiner, and D. Wuillemin
High-Temperature Solar Technology, Paul Scherrer Institute, 5232 Villigen PSI/Switzerland

Concentrated solar radiation provides unique opportunities to study chemical and physical phenomena under conditions that are difficult to achieve by conventional techniques: Particulate samples can be heated up to temperatures higher than 2000 K within a few millisecond, or cm^2-sized samples can be continuously maintained at such temperatures with temperatures dropping within some millimeters at the border of the exposed area. The art is to tame this powerful source by building suitable devices and to employ it in controlled experiments. In order to advance the science of converting solar radiation into solar fuels, we aimed at utilizing concentrated solar radiation for studying the decomposition of mixed iron oxides $Fe_{3-x}M_xO_4$ (M=Mn, Mg; $x^2 1$).

The first research tool presented herein was devised to investigate the decomposition of µm-sized oxide particles with reaction times in the range of less than 100 ms under controlled atmospheres. The device is essentially a tubular cavity that is closed with a quartz window. Heating of the particles is achieved by direct absorption of concentrated solar radiation in a particle/gas suspension (powder cloud). The reactants are continuously fed to the reaction zone through a preheating section. After passing the reaction zone the particles are quenched and collected. The presence of lower valence oxides $Fe_{1-x}M_xO$ in exposed samples indicates that the particles reached temperatures up to 2100 K within less than about 50 ms. This device appears to be generally applicable for exploring fast gas/solid or decomposition reactions that are of qualitative or exploratory character. The second research tool we present was designed to conduct batch experiments under controlled atmospheres with metal oxides in the solid or the liquid state. Reaction times may vary between 0.3 to several minutes. The sample is placed on a water-cooled support from copper to avoid any reaction between the oxide and the support. Exposure to concentrated solar radiation results in sample temperatures up to 2100 K within a few seconds.The course of the reaction can be monitored by collecting evolved gases with a capillary and analyzing them in a mass spectrometer. Information about the high-temperature composition of the sample can be obtained from analyses of quenched samples. Temperatures are measured, e.g., by means of flash-assisted multiwavelength pyrometry (FAMP). Atmosphere control, gas analytics and temperature measurement provided an excellent set-up for kinetic investigations on the decomposition of manganese oxide. The use of this device for conducting similar studies, e.g., for high-performance ceramics, such as silicides or nitrides, can easily be envisioned.

O24

Evaporation of Boron-, Silicon- and Titanium-doped Carbon Materials

E. Vietzke, K. Flaskamp, M. Hennes

Institut für Plasmaphysik, Forschungszentrum Jülich GmbH, Euratom Association,
Trilateral Euregio Cluster, D-52425 Jülich, Germany

In fusion devices, the plasma-facing materials have to withstand high heat fluxes. In present day tokamaks, graphite-based materials are used due to their good thermo-mechanical properties and their low atomic number Z. These materials show no melting and a thermal sublimation becoming considerable only above 2400 K. However, erosion due to plasma ion impact is high for all low-Z materials and, especially for carbon, the chemical reactivity with hydrogen and oxygen atoms and ions further enhances the erosion. This limits the lifetime of the components and dilutes the plasma with impurity ions.

The reactivity of carbon in metallic carbides with hydrogen and oxygen is strongly reduced. Therefore, attempts to save the good thermo-mechanical properties of graphite and to reduce his chemical erosion with hydrogen and oxygen have led to the introduction of dopants into the carbon matrix or on the carbon surface of plasma-facing components. Indeed, such modifications ("boronization" and "siliconization") have highly improved the plasma performance. The thermal behavior of such doped carbon material is important for its use in fusion devices. The deposition of high heat load pulses can lead to additional erosion by evaporation or to a loss of preferential properties of the doped carbon material.

In this contribution, evaporation rates up to 2300 K from some doped carbon materials foreseen for an use as high heat load components in fusion devices have been measured: boron-doped graphite CL1122(4%B), Si-doped SiC30 (30% Si), Ti-doped RG-Ti (2 at% Ti), a-C/Si:H film from siliconization in TEXTOR.

The B and Ti sublimation from these doped graphites is reduced compared to pure B or Ti material, being similar to the corresponding carbide. In the case of SiC30 with a the free Si component (4 at%, in islands) the Si evaporation is similar to pure Si, after a heat treatment up to 2000 K also similar to SiC. Films from the siliconization of TEXTOR walls show a Si sublimation rate between pure Si and SiC.

GROWTH OF METAL CLUSTERS IN MATRICES

Andreas Kornath, Alexander Kaufmann, Anja Zoermer, Ralf Ludwig
Universität Dortmund, Fachbereich Chemie, D-44221 Dortmund, Germany

Naked (free of ligands) alkaline metal clusters are a favored topic of theoretical investigation and the development of models about the structure and properties of atomic metal clusters. Despite considerable recent effort, the structures of small atomic metal clusters remain largely unexplored by experimental methods. This is not only due to the intrinsic difficulties associated with the generation of the unstable species, but also due to the lack of experimental methods which may provide a way to determine the cluster geometry.[1,2]

Recently this problem has been solved by the development of the multi channel Raman matrix spectroscopy.[3-8] This technique allows the direct observation of the vibrational frequencies of small metal clusters. Correlation of the experimental data with theoretical methods (density functional calculations) provides a reliable way to determine the geometry and bonding of atomic clusters. Furthermore, the technique allows monitoring of the cluster growth in rare gas matrices during annealing procedures. The experiments show that the cluster growth during this process does not proceed random-like but is dominated by the formation of relatively stable species. The formation of the rhombic K_4 and Na_4 clusters is one example. Another example is the formation of green Na_8 clusters from blue Na_4 clusters. The hypertetrahedral octasodium is the first isolated magic number cluster, whose enhanced stability was predicted by the Jellium model.

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O26

Matrix Isolation of Boron and Carbon Vapor.
Control of Cluster Formation during Preparation and Annealing.

Carl William Larson, Air Force Research Laboratory,
Edwards AFB, CA 93524-7680, Email: carl_larson@ple.af.mil

Boron and carbon vapors were produced with a resistively heated oven (~ 3000 K) and co-condensed with 100- to 1000-fold excess argon on a CsI or BaF2 substrate maintained at ~ 10 K. A series of matrices were studied where the B/C ratio varied from zero to about 10. Matrices were repeatedly annealed to a constant composition at ~30 K and analyzed by Fourier TransformInfrared spectroscopy. Quantitative analysis was carried out with use of Beer's law, measured absor-bances, A(i), and absolute infrared absorption intensities, I(i), obtained from ab-initio theory, viz., r(i) = A(i)/I(i), where r(i) is the column density of the ith species. Annealing of pure carbon matrices led to disappearance of atoms, dimers and trimers from the initial deposits. The identified products of recombination included cyclic C6 and cyclic C8, and linear Cn molecules, 4 W n <13. After annealing to constant composition, the total measurable carbon was found to be as much as twice the initial measurable carbon, indicating that about 50 % of the initially deposited carbon was isolated as atoms and dimers. The cyclic molecules, the dominant condensation products, amounted to as much as ~ 60% of total carbon in the fully annealed matrix. In matrices containing boron, linear C3 and cyclic BC2, B2C, and B3, constituted about 80% of the total observable boron and carbon in the initially deposited matrix. Statistical substitution of J boron atoms into an n-atom carbon cluster produces a distribution given by r(BJCn-J)/ r(Cn) =[n!/J!(n-J)!] [B/C]J. Obser-vation of approxi-mately statistical distributions in clusters with n = 3, 4, and 5 in the initially deposited matrices implies that these smaller clusters form by random condensation of well-mixed atoms, uninfluenced by their relative energies, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics. B2Cn-2 clusters, once formed, were inert to further condensation upon annealing. Thus, energy loss by recombination during preparation of high energy density matrices (HEDM) is minimized in matrices with large B/C ratios. For example, when B/C ~2, any recombination that does occur during co-deposition would tend to produce B2C, which is an inert molecule. In pure boron HEDM, the cyclic B3 molecule may be similarly inert, which would suggest that energy loss by recombination will also stop at a B3 "island of stability." Experimental work to produce five mole percent pure boron HEDM is concentrating on development of a novel high-flux boron atom source, the "boron cannon," and use of UV-VIS and FTIR spectroscopy to characterize the source and the HEDM matrix.

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The Air Force High Energy Density Matter (HEDM) program supported this research.

O27

Structure and Bonding of Hyperlithiated Molecules $Li_n(OH)_{n-1}$ (n = 2-5) Generated by Laser Ablation of Slightly Oxidized Lithium

Hiroshi Kudo[1], Hiromasa Tnaka[1] and Keiich Yokoyama[2]

[1] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

[2] Department of Materials Science, Japan Atomic Energy Research Institute, Tokai-mura 319-1195, Japan

Abstract

Since the first observation of a "hyperlithiated" Li_3O molecule in the equilibrium vapor over $Li_2O(s)$ at elevated temperatures [1], we have extended experimental and theoretical studies on the structure and bonding of hyperlithiated or hypervalent molecules like CLi_6, Li_4O, Li_3S, Li_4S, Li_4P, Li_2CN, Na_2CN and K_2CN [2-6]. In the present work, we have detected molecular species $Li_n(OH)_{n-1}$ (n = 2-5) with a time-of-flight (TOF) mass spectrometer in a pulsed molecular beam generated by laser ablation of slightly oxidized lithium metal. The ionization energies determined by photoionization were 4.32 ± 0.08 eV for Li_2OH, 4.10 ± 0.05 eV for $Li_3(OH)_2$, 3.29 ± 0.1 eV for $Li_4(OH)_3$ and 3.58 eV for $Li_5(OH)_4$. The observed values agreed reasonably well with the theoretical values 4.49, 3.57, 3.40 and 3.05 eV, respectively, calculated by the CCSD(T)//B3LYP/6-311+G* or MP2//B3LYP/6-311+G** level. We have also obtained the precise ionization energy 3.59 ± 0.02 eV for Li_3O, the theoretical value of which is 3.57 eV.

Thus obtained ionization energies yield clues to the stable structures of Li_2OH and $Li_3(OH)_2$ as well as Li_3O; the density functional theory (DTF) calculation at B3LYP/6-311+G** gives some structural isomers for each species. We discuss the nature of bonding of these hyperlithiated molecules based on the experimental results as well as theoretical calculations of the electronic structures and charge populations.

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O28

Evaporation and Condensation Coefficients by the Multiple Knudsen Cell Mass Spectrometric Method

C. Chatillon, LTPCM/ENSEEG - CNRS (UMR 5614, INPG-UJF), BP.75 38402 Saint Martin d'Hères - France

Low kinetic vaporization rates occuring in Knudsen cells lead to a decrease in measured pressures that can be used to determine the so-called evaporation coefficient α. Total α values are usually determined by thermobalance or torsion effusion applied to free vaporization. Coupling a mass spectrometer to such devices allows the direct determination of the α coefficient of each gaseous species, but there remains some experimental difficulties related to surface temperature accuracy and mass spectrometer calibration. Consequently, use of effusion cells with different orifice size and Motzfeld relation (1955) appears more convenient. Depending on the α value and of the cell geometry - i.e. the ratio f between the effective effusion area sC and the vaporizing cross-section S of the cell - the usual Motzfeld relation, $p_{eq} = p_m (1 + f/\alpha)$ shows that measured pressures p_m may be slightly different from equilibrium pressures p_{eq}. Such small differences may become difficult to measure using conventional Knudsen-cell mass spectrometry and to assign to the lone orifice size effect. Consequently, we have used for the first time the Multiple Knudsen Cell Mass Spectrometric Method to determine α_{SiO} for {Si + SiO_2} or {SiO, am} samples (Rocabois et al. 1992-93). For compounds with very low α values, as for example α_{N2} measured on Si_3N_4, use of extrapolated pressure values to f = 0 (or s = 0) did not logically lead to the known equilibrium pressure and this feature may be attributed either to change in the kinetic process (Rosenblatt 1963) or to the existence of a condensation coefficient β different from α (Chatillon et al. 1999) and the Motzfeld relation must be modified. α and β coefficients were determined for SiC, SiO_2 and Si_3N_4 compounds as for their mixtures (Chatillon et al. 1999, Rocabois et al. 1999). This analysis is also applied to multicomponent systems, as for instance the sintering of SiC with Al_2O_3/Y_2O_3 additives.

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Thermochemical Studies of Oxide Ceramics Using An Atmosphere-Controlled High Temperature Mass Spectrometer

M. Yamawaki, K. Yamaguchi, J. Huang, A. Suzuki,
M. Yasumoto and H. Sakurai
Graduate School of Engineering, University of Tokyo 7-3-1 Hongo,
Bunkyo-ku, Tokyo 113-8656 Japan

A new system to introduce mixed gas into a Kundsen cell from outside high temperature mass spectrometer has been developed. By using this system, the reaction equilibria between oxide ceramics and reactive gases of 0.1-1 Pa of pressure were measured at high temperatures. First, lithium vapor losses from lithium oxide ceramics, candidate material for tritium breeder, were evaluated for the sweep gas of helium added with 0.1% hydrogen, such as designed for a fusion reactor blanket. Generally, hydrogen addition to the sweep gas was confirmed to enhance the lithium loss substantially. Second, potential release and transportation of strong radioactive fission products, Cs, Sr and Ba, in a severe accident of the nuclear reactors were evaluated by measuring the vapor pressures of UO_2-based complex oxides with Cs, Sr or Ba in an atmosphere containing low pressure D_2/D_2O. It was observed that cesium pressure increases with hydrogen addition to cesium uranates, while strontium and barium pressures decrease with hydrogen addition to their uranates.

O30

KC-MS and FTIR Matrix Isolation Study of Manganese Oxyfluoride Species

G.Balducci [a], M.Campodonico [a], G.Gigli [a], S. Nunziante Cesaro [b]

[a] Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A.Moro 5,
I-00185 Roma,Italy
[a] CNR-CSTCAT, c/o Dipartimento di Chimica, Università di Roma "La Sapienza"
P.le A.Moro 5, I-00185 Roma, Italy

Thermochemical data are scarce or completely lacking for ternary gaseous species such as mixed oxo-halides of many transition metals, in particular of the I main series. Yet, these data are very useful when modeling many high temperature processes.

Knudsen cell-mass spectrometric experiments were recently carried out on the vaporization of mixtures of Mn oxides at various stoichiometric compositions with Mn difluoride which led to a first identification of the molecules MnFO(g) and $MnOF_2$ (g). Suitable experimental conditions have been attained where all-gas equilibria involving the pertinent species could be studied.

From second-law and third-law analysis of the equilibrium data the atomization energies of MnOF(g) and $MnOF_2$ (g) were evaluated.

Concurrently, FTIR-matrix isolation experiments were carried out in order to get clues on the vibrational features of the Mn-O-F species. The vapors produced in effusive conditions by vaporizing mixtures on Mn oxides with MnF_2 or MnF_3 have been trapped in argon cage. In the conditions of the experiments so far realized the bands observed at 988.4, 692.3 and 683.7 cm-1 were tentatively assigned to stretching modes of the $MnOF_2$ molecule.

On the basis of the experimental data obtained and other estimated molecular parameters sets of thermodynamic functions were calculated for $MnOF_2$ and MnOF which were then employed in the evaluation of the pertinent equilibria.

O31

Kinetic studies on the oxidation of Fe-Si steels in the temperature range from 1000 - 1400 °C

M.Spiegel, H.J.Grabke and K.H. Tacke

Max-Planck-Institut für Eisenforschung GmbH
Max-Planck-Str.1, 40237 Düsseldorf
Germany

The formation of oxide scales on steels, growing during the twin roll thin strip casting technology leads to significant product quality problems and has a significant impact on process yields and economics. The thin strip casting of steel in the thickness range of 1 ñ 5 mm is an important current development in casting technology, promising large savings of energy and equipment compared to conventional casting techniques. The aim of this work is to investigate the kinetics of scale formation and the determination of the process parameters, required for the reduction of scale growth during the casting process. The major part of the scale is formed in the first minutes of the casting process, when the metal temperature is close to its melting point. Short term thermogravimetric studies (up to 1 h) were carried out on Fe-1.7 wt.% Si and Fe-3.46 wt.% Si in the temperature range from 1000 ñ 1400 °C in synthetic air at constant flow rate. At 1000 °C the oxidation of both alloys follows the parabolic rate law, and Fe.1.7 Si oxidizes much faster than Fe-3.46 Si. In both cases a doublelayered scale of Fe2O3 and Fe3O4 is formed, for Fe-3.46 Si also a Si-enriched zone was identified underneath the oxide scale. At 1100 °C the oxidation rate of Fe-1.7 Si turns to be linear, whereas the kinetics of oxide growth on Fe-3.46 Si is still parabolic. At 1200 and 1400 °C a dramatic increase in mass gain takes place for both alloys compared to 1100 °C and the corrosion rate of Fe-3.46 Si also turns to be linear. In this temperature range the mass gain is nearly independant of temperature and composition of the alloy. Investigation of the corroded samples after the experiments have shown the formation of a molten phase at the scale/metal interface. As diffusion processes through the molten phase are very fast, the kinetics of corrosion is probably determined by diffusion of oxygen in the gas phase through the laminar boundary layer. More short term experiments will be conducted at 1400 °C on the influence of p(O2), water vapour and the flow rate of the gas.

O32

Interfacial Engineering for Oxidation Resistant Alloys

K. Prüßner[*], **B.A. Pint, K.B. Alexander**[#], **and P.F. Tortorelli**

Oak Ridge National Laboratory, Oak Ridge, TN, USA
[*]now at: Institut für Werkstofftechnik, Universität Siegen, Germany
[#]now at: Los Alamos National Laboratory, Los Alamos, NM, USA

Materials for use under high temperature conditions often suffer from corrosion due to the interaction with the gaseous environment. Reasonable lifetimes under service conditions can only be achieved if a dense and well adherent oxide scale is formed to prevent further degradation of the material. Therefore the adhesion of the oxide scale is critical for the performance. A similar case is the adhesion of thermal barrier coatings (TBCs), where an oxide scale grows between the bond coat and the thermal barrier coating, which can limit the lifetime of the component.

In our experiments we have studied both technical alloys and model materials to determine factors affecting the adhesion of scales and coatings on high-temperature alloys. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) including energy-dispersive X-ray spectroscopy (EDS) were used to study the oxidation performance and to characterise the microstructure and microchemistry of scales and coatings.

It could be shown that the composition of the scale/alloy interface is a critical parameter for optimising the oxidation performance. Alloys which contained additions of small amounts of "reactive elements" exhibited in all cases a better oxidation performance than alloys of the same base composition without this addition. Studies of the interfacial chemistry revealed that the reactive element segregates to the scale/metal interface and to oxide grain boundaries. In alloys without a reactive element sulfur is found at the interface. Doping of alloys with additional sulfur resulted in further deterioration of the oxidation performance and for higher sulfur concentrations segregation of sulfur at grain boundaries in the oxide scale was also found. Similar effects were observed for thermally grown oxide scale, deposited coatings of similar composition and oxide scales grown between thermal barrier coatings and bond coats.

O33

REFRACTORY CARBIDES / OXYGEN INTERACTION AT LOW PRESSURES AND HIGH TEMPERATURE

P.L. Cignini*, D. Gozzi& and S. Shimada#
Dipartimento di Chimica, Università di Roma *La Sapienza*
P.le Aldo Moro 5, 00185- Roma, Italy

The reactivity of NbC (single crystal and sintered samples), TiC (single crystal and sintered samples) and sintered ZrC in the temperature range from ambient to 1020 °C and at oxygen partial pressures from 0.07 to 9 Pa will be reported. The reactivity of the principal (hkl) orientations of TiC as well as the sintered samples have been also measured at 0.8 Pa of O_2. At given experimental conditions, it has been found that the oxidation of TiC (110) single crystal produces the growth of epitaxial rutile. This is the starting pont for studying the electronic properties of the MeC/MeO junctions. Preliminary information can be obtained through the combined measurements of reactivity and "in situ" electrical resistivity. Measurements on sintered samples of TiC and ZrC, both as received and high temperature-high vacuum treated, will be also presented. Large differences in the reactivity hystereses have been found.

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* CNR-CSTCAT, c/o Dipartimento di Chimica, Università di Roma *La Sapienza*
&Corresponding author. Email.:gozzi@axcasp.caspur.it
Department of Materials Science, Faculty of Engineering, University of Hokkaido, Sapporo, Japan

O34

Deformation phenomena accompanying internal precipitation in solids

A. A. Kodentsov, M.J.H. van Dal, C. Cserháti and F.J.J. van Loo
Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

There is now ample experimental evidence to support the view that the net volume increase accompanying an internal reaction in solid materials may result in a number of deformation phenomena including creep and grain boundary sliding.

Internal nitridation of dilute Ni-based alloys (viz. Ni 5at.% Cr and Ni 1.5at.%Ti) at 500-700°and high fugacities of nitrogen (under flowing NH_3+H_2-gas mixture) is considered as an example. Under these conditions the overall uptake of nitrogen by the alloys is controlled by nitrogen diffusion in the metal. Solute atoms (Cr or Ti) are precipitated out completely at the reaction front and the formation of semi-coherent nitride particles takes place.

A volume change associated with the precipitation reaction result in a stress gradient between the alloy surface and the internal nitridation front. It was observed that stress relief occurred mainly by transport of nickel (solvent metal) to the gas/metal interface, leading to pure Ni at the surface. Pipe diffusion-controlled creep appeared to be the dominant stress accommodation mechanism. This mechanism is prevailing because of a large dislocation densities generated in the Ni-matrix upon the internal precipitation of the semi-coherent nitride particles.

These mechanical aspects of the interaction cannot, at this moment, be incorporated into the existing theories of the internal precipitation. However, they might also play an important role and, even, be under certain conditions rate-limiting for the overall process.

Y and Zr Tracer Diffusion in Yttria-Stabilized Zirconia at Temperatures Between 1800 K and 2050 K

M. Kilo(1), G. Borchardt(1), B. Lesage(2), S. Weber(3), S. Scherrer(3)

(1) Institut für Allgemeine Metallurgie, TU Clausthal, Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany

(2) Laboratoire d'Étude des Matériaux Hors Équilibre (LEMHT) CNRS ESA 8072, Bât. 410, Université Paris-Sud XI, Orsay, F-91405 Orsay Cedex, France

(3) Laboratoire de Physique des Matériaux, École des Mines Nancy, Parc de Saurupt, F-54042 Nancy Cedex, France

Tracer diffusion of both yttrium and zirconium in single crystalline YSZ (YSZ: yttria stabilized zirconia; containing 10 to 32 mol % Y_2O_3) were measured at elevated temperatures ($1800\ K < T < 2050\ K$) using rare isotopes. For zirconium diffusion, the stable isotope ^{96}Zr was used, and the samples were analysed using secondary ion mass spectroscopy. In the case of the yttrium diffusion, the radioactive tracer ^{88}Y was used, and a sectioning technique was applied.

The zirconium tracer diffusion is slower as the yttrium tracer diffusion, and from the dependency of the diffusivity on the yttria concentration was also evaluated: the zirconium tracer diffusion coefficient decreases with increasing yttria content. From the activation enthalpy (4.6-5.4 eV) and concentration dependence of the cation diffusion, it is concluded that the cation diffusion occurs via free vacancies ($V_{Zr}^{4'}$).

The results are compared to those obtained earlier in this system at temperatures below 1750 K, and to the observations in the calcium stabilized zirconia.

O36

Preparation, Characterisation and Cation Diffusion in polycrystalline $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$

O. Schulz, M. Martin

Institute of Physical Chemistry, Darmstadt University of Technology
Petersenstraße 20, 64287 Darmstadt, Germany

Dense samples with a well defined distribution of grain sizes are essential for the investigation of diffusion or degradation processes in polycrystalline SOFC-components. The precursor based Pechini method [1] was found to be suitable for these puposes. Polycrystalline samples of Lanthanumgallate, doped with strontium on A- and magnesium on B-sites, $La_{1-X}Sr_XGa_{1-Y}Mg_YO_{3-(X+Y)/2}$ (LSGM), were prepared using this method. Characterization by x-ray diffraction (XRD) showed that the resulting samples, which are annealed at 1400°C in air are single phased. Using in situ XRD measurements the dissociation and crystallization of the amorphous precursor powders of the Pechini preparation was followed up to 1100°C.

Results for the cation diffusion coefficients of different cations at T=1400°C were obtained by the radiotracer sectioning method and SIMS (Secondary Ion Mass Spectrometry). Two different mechanisms (grain boundary and bulk diffusion) were found and ratios of grain boundary to bulk diffusion coefficients had been obtained. Temperature dependence of diffusion was investigated for temperatures down to 1100°C.

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O37

DEPOSITION KINETICS OF TIB_2 FROM $TICL_4$-BCL_3-H_2-HCL GAS MIXTURES BY THERMAL CVD IN A HOT-WALL REACTOR

Ch.-Ho Yu, E. Zimmermann, D. Neuschütz

Lehrstuhl für Theoretische Hüttenkunde,
Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen
D-52056 Aachen, Germany
Phone: ++49-241-80-5966, Fax: ++49-241-8888-295
e-mail: neuschuetz@lth.rwth-aachen.de

Abstract: The deposition rate of TiB_2 was measured in a hot-wall CVD reactor by means of a thermobalance at 1 bar in the temperature range 800 to 950°C at variable partial pressures of $TiCl_4$, BCl_3, H_2 and HCl. HCl additions proved to have a retarding effect on the deposition. From the temperature and the flow rate dependence of the deposition rate it was concluded that the process was determined by chemical reactions rather than gas diffusion. The deposition rate was found to be proportional to the feed gas partial pressures p_i^0 of $TiCl_4$ and BCl_3 at low partial pressures. After a rate maximum the rate decreased with rising $p°(TiCl_4)$ and $p°(BCl_3)$. The maximum of the deposition rate described as a function of the $BCl_3/TiCl_4$ ratio in the feed gas changed with rising $p°(TiCl_4)$. Above a $BCl_3/TiCl_4$ ratio of 5 the deposit became rough. The deposition rate increased with the feed gas partial pressure of H_2 and decreased with rising HCl contents. The experimental results point towards a complex reaction mechanism determined by more than one reaction step and possibly influenced also by transport processes. The measured reaction rates are tentatively interpreted by a reaction model and reproduced by means of numerical simulation.

O38

Pulsed laser ablation deposition of ZrC films

G. De Mariaa, L.DíAlessiob, D.Ferroc , R.Teghilb

a ìUniversit‡ ìLa Sapienzaî, P.le A.Moro 5-00185 ROMA ITALIA
b Universit‡ della Basilicata , Via Nazario Sauro 85-85100 POTENZA ITALIA
c CNR Centro per la Termodinamica Chimica alle alte Temperature- P.le A.Moro 5- 00185 ROMA ITALIA

At the present time thin films of refractory compounds were widely applied as wear-resistant coatings in the cemented carbide industry. In particular titanium carbide is a semimetallic ceramic with some peculiar properties as high thermal stability, hardness and corrosion resistance .

Zirconium carbide films prepared by pulsed laser ablation technique, starting from hot pressed ZrC pellets evaporated by Frequency Doubled Nd-YAG laser, were deposited on silicon [111] in a vacuum chamber under different experimental conditions.

Different analytical techniques were utilised to obtain informations about the gaseous and solid phases during the processing.

In particular the gaseous phase has been characterised by mass spectrometry, emission spectroscopy and geometrical distribution .

A critical evaluation of the results has been studied to verify eventual different deposition behaviour as a function of different ranges of the laser fluence.

X-Ray diffraction and XPS analyses give indications about the composition and cristallinity grade of the films .

The deposited obtained varying the process experimental conditions have been characterized also as regards their mechanical properties of hardness by using a metodo that allow to derive the films hardness from indentation measurements of the system substrate -film.

. From the analytical results and the thermodynamic considerations, the experimental conditions to optimise the ablation process parameters, for the ZrC films preparations, were derived.

O39

OXYGEN PERMEATION THROUGH MIXED CONDUCTING OXIDE MEMBRANES

Michael Schroeder[a], Keqin Q. Huang, and John B. Goodenough

Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712-1063,USA
[a] On leave from: *Institut fuer Physikalische Chemie - Elektrochemie, TU Darmstadt, Petersenstrasse 20, 64289 Darmstadt, Germany*

The continuous electrosynthesis of syn-gas (CO + H_2) via ceramic membranes is considered an important technology in the field of energy conversion because it provides an efficient alternative for transforming natural gas into liquid fuel. The basic function of the membrane is to provide a controlled 'leak' of oxygen that is needed to oxidize the methane. The membrane material of choice should meet the following critera:

- Exhibits mixed electron and oxide-ion conductivity and fast surface exchange reactions in order to assure a high oxygen permeation flux through the membrane.
- Is stable at low oxygen partial pressures and in actively reducing environments containing H_2 and CO.
- Has high catalytic activity for the formation of syn-gas and is a low cost material.

In recent years, two concepts have been pursued to find suitable membrane materials: a) The use of homogeneous mixed conductors (MIEC) with perovskite structure [1] and b) dual phase materials containing a phase with high electronic conductivity (e.g. a noble metal) and a second phase that is a good ionic but poor electronic conductor (e.g. yttria doped zirconia) [2, 3]. The dual phase materials are stable even in reducing environments. On the other hand, homogeneous MIEC like $La_{1-x}Sr_xCo_{1-y}B_yO_{3-\delta}$ (B = Co, Fe, Ni) produce higher oxygen permeation fluxes at lower costs but undergo significant reduction at reduced oxygen partial pressures. We introduce a new concept by using a perovskite MIEC with a thin protective layer (d = 1 µm) of Samarium doped ceria $Ce_{1-x}Sm_xO_{2-\delta}$, which is stable at low $p(O_2)$. When the membrane is operated with the layer being exposed to reducing gas atmospheres, the Ce^{4+}/Ce^{3+} redox couple is believed to provide enough electrons to facilitate the oxygen permeation. With coated membranes, stable permeation fluxes were achieved in oxygen permeation experiments lasting for more than 300 hours whereas uncoated membranes degraded quickly. The protective effect and the permeation flux through the coated membranes are discussed in the light of the electronic and ionic conductivities of layer and substrate.

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O40

Increased Cathode Performance using a Thin Film LSM Layer on a structured 8YSZ Electrolyte Surface

D. Herbstritt*, U.Guntow°, A. Weber*, G. Müller° and E. Ivers-Tiffée*

* Institut für Werkstoffe der Elektrotechnik IWE
Universität Karlsruhe (TH)
Adenauerring 20, 76131 Karlsruhe, Germany
° Fraunhofer Institut für Silicatforschung ISC
Neunerplatz 2, 97082 Würzburg, Germany

A considerable part of the power losses in a SOFC single cell occurs due to the polarization resistance of the cathode / electrolyte interface. The high cathodic overvoltage occurring at sufficient average current densities lead to a decreased efficiency and an enhanced degradation of the cell. Therefore the development of a cathode with a small polarization resistance and sufficient long term stability is an important goal. In case of a screen printed LSM cathode layer (LSM: $La_{1-x}Sr_xMnO_3$) on a YSZ electrolyte substrate (YSZ: Y_2O_3 doped ZrO_2) the cathodic reaction is generally assumed to be restricted to the three phase boundary between cathode, oxidant and the electrolyte surface. One method to increase this electrochemical active area is to increase the cathode/electrolyte interface by interlocking electrolyte and cathode. A well defined, three dimensional interface was realized by structuring the electrolyte surface via screenprinting a porous monolayer of individual 8YSZ-particles (particle size $\approx$ 17 µm) onto the electrolyte substrate. The structured electrolyte surface was covered with a thin LSM MOD layer (MOD: metallo-organic-deposition, approx. 80 nm thick). Finally a screen printed LSM layer was applied as a current collector. This microporous LSM MOD layer exhibits a large amount of three phase boundaries. Therefore the cathodic reaction can take place all over the enlarged electrolyte surface, resulting in a decrease in the polarization resistance. Single cells with these modified cathodes showed a power output of about 0.8 W/cm² at 0.7 V cell voltage whereas a cell with a standard LSM-cathode achieves a power output of about 0.35 W/cm² at the same operating conditions (950 °C; oxidant: air, 0.7 l/min; fuel: hydrogen, 0.5 l/min, 15 % fuel utilization).

041

Atomistic Diffusion Mechanism in High Temperature Proton Conductors

R. Hempelmann
Physikalische Chemie, Universität des Saarlandes
D-66123 Saarbrücken, Germany

Some perovskite type oxides with extrinsic vacancies on their oxygen sublattice dissociatively dissolve water from the gas phase and thus become good protonic conductors at elevated temperatures. We have studied this conductivity by in-situ impedance spectroscopy. Further macroscopic measurements concern the thermodynamics of water absorption; we have recorded pressure/composition isotherms ex-situ by Nuclear Resonance Reaction Analysis, which we interpret in terms of a two state model based on Fermi-Dirac-Statistics [1]. Microscopically we have elucidated the mechanism of proton diffusivity and thus conductivity by means of Quasielastic Neutron Scattering [2] and Muon Spin Relaxation [3]. Again we observe two diffusional proton states. Our microscopic and macroscopic results are in mutual agreement and support each other.

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Short Presentations

S 1 – S 7

S1

DEMONSTRATION OF FACTSage AND ChemApp at HTMC-X

Arthur D. Pelton, Christopher W. Bale,
Centre de Recherche en Calcul
Thermochimique,
Ecole Polytechnique,
Montreal, Quebec H3C 3A7, Canada

Gunnar Eriksson, Klaus Hack, Stephan
Petersen
GTT-Technologies
Herzogenrath, Germany

Pertti Koukkari
VTT CHEMICAL TECHNOLOGY
Helsinki, Finland

FACTSage (Facility for the Analysis of Chemical Thermodynamics using the SOLGASMIX-based advanced Gibbs Energy Minimizer) is an integrated thermodynamic database computing system used extensively in the metallurgical, materials and chemical engineering industries.

FACTSage offers access to the Pure Substances databases, compiled and assessed by the FACT group and by SGTE, which together cover data for more than 5500 stoichiometric compounds. It also permits access to the Solution databases assessed by FACT and SGTE. The FACT databases include non-ideal solutions for such varied systems as oxide melts/glasses, crystalline ceramics, molten and solid salts, dilute metallic solutions and aqueous solutions. The SGTE databases cover non-ideal solutions in metal-metal, metal-carbon-nitrogen and many other liquid and solid alloy systems.

The FACTSage software, which automatically accesses these databases, calculates multiphase, multicomponent equilibria by Gibbs energy minimization. Modules for the calculation of point equilibria and one-dimensional phase maps are available. A new module for two-dimensional phase mapping permits the calculation of a multitude of different kinds of phase diagrams. FACTSage functions on Windows 95, 98 or NT and comes with a wide range of graphics (e.g. phase diagram plotting) and spreadsheet capabilities.

ChemApp is a thermochemistry library for your own software development. It allows you to perform equilibrium calculations by Gibbs energy minimization from within your own or third party software. This enables simulation calculations which may also incorporate kinetic modeling in conjunction with thermodynamic equilibrium calculations. ChemApp uses the same Gibbs energy minimization software as does FACTSage. ChemApp data files can be created automatically with the FACTSage software from the FACT and/or SGTE databases.

A very special application of ChemApp called ChemSheet will also be demonstrated. ChemSheet combines the flexibility and practicality of spreadsheet applications with rigorous, multiphase thermodynamic calculations. Each application is defined as an independent worksheet in ExcelR, in which the entire simulation can be performed.

FACTSage, ChemApp and ChemSheet will be demonstrated, and conferees will be offered hands-on use on computers supplied by the Conference. Conferees bringing their own lap-tops will receive free copies of FACTSage-Demo, ChemApp-light, and a demo-version of ChemSheet.

S2

Thermo-Calc and DICTRA in Assisting Materials Design

Bo Sundman[1], **John Ågren**[1], **Pingfang Shi**[2]

[1] Department of Materials Science and Technology
Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[2] Thermo-Calc AB, Stockholm Technology ParkSE-113 47 Stockholm, Sweden

Quantitative conceptual design of various materials has been tremendously benefited from computational calculations and simulations in the last decade [1,2]. The Thermo-Calc [3, 4] and DICTRA [5,6] software/database packages, which have been developed over the past 25 years, have a comprehensive combination of thermodynamic and kinetic models that make it possible to predict material compositions, structures and properties resulted from various material processes. The two packages have aimed at providing various materials scientists and engineers with engineering tools in their daily work of materials research and development.

Thermo-Calc is one of the most common software in the field of Computational Thermodynamics, which can calculate complicated heterogeneous phase equilibria and multicomponent phase diagrams. DICTRA is probably the only software available in the market now which can precisely simulate DIffusion-Controlled phase TRAnsformation in various materials. DICTRA uses Thermo-Calc as its engine for thermodynamic calculations, but extends to applications with kinetic problems engaged.

Both software have been connected with many high-quality thermodynamic and kinetic databases, which are useful for various applications in R&D of steels, alloys (Al-/Ti-/Ni-/Mg-/Cu-based and others), hard materials, ceramics, slags, molten slats, recycling, sintering, semi-/super-conductors, ploymers, solders, car industries, food production, energy transfer, Earth materials, environmental protection, and so on. They are renowned for their most powerful facilities, flexible third-party programming interfaces and user-friendly graphic interfaces.

Many applications have demonstrated their great capacities in calculating material properties and simulating material processes [7-11]. Some successful examples of using these software, databases and application programming interfaces in assisting materials design will be shown in this presentation. Also be given will be some discussions on the further development of the Thermo-Calc and DICTRA software/databases in future.

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S3

MTDATA - The NPL Tool for Materials Thermochemistry

R H Davies, A T Dinsdale, J A Gisby, S M Martin, J A J Robinson
National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK

Abstract

MTDATA has long been one of the world's foremost thermochemical modelling packages. Developed at the National Physical Laboratory (NPL) it has proved itself over many years of use in solving practical problems. It is a powerful and user-friendly software and data package for the prediction of phase equilibria in systems containing large numbers of chemical elements. MTDATA is leased to industrial, government and academic organisations world-wide and training courses are held regularly at NPL and in the US.

It has numerous applications in the fields of metallurgy, chemistry, materials science, and geochemistry depending only on the data available. Problems of mixed character can be handled, for example equilibria involving the interaction between liquid and solid alloys and matte, slag and gas phases. MTDATA has been designed around the high reliability of the NPL *Numerical Optimization Software Library*. This means that no start points are required for a given problem - MTDATA will find automatically the conditions which give the minimum in the Gibbs energy.

The main platform for MTDATA is Windows (95, 98 and NT). MTDATA for Windows combines the power and reliability of the core of MTDATA with the ease of use and versatility of Windows. With just a few simple clicks of the mouse it is possible to calculate a phase diagram, compute a series of complex equilibria, or examine the thermochemical properties of multicomponent industrial alloys. Windows standards of consistency and compatibility including use of context-sensitive help, multi-tasking and printer support, mean that MTDATA for Windows is as intuitive and accessible for occasional users as it is for regular users. Interactive "click and go" graphical control has been built in to enable the calculation of binary and ternary phase diagrams to be especially easy. Versions of MTDATA are also available for most UNIX platforms, VMS alpha and VAX, and for MS-DOS and utilise a flexible and powerful character based interface.

A range of databases covering a wide variety of system types is offered for use with MTDATA although experienced users may wish to create and manage their own. A large number of databases may be used at any one time. Those available for use with MTDATA include the databases developed by SGTE, a consortium of eleven European centres concerned with the development of thermodynamic databases for inorganic and metallurgical systems and their application to practical problems. NPL is a founder member of SGTE.

Incorporated within MTDATA is the capability to handle a wide range of thermodynamic models to represent the effects of temperature, pressure and phase composition on Gibbs energies. These can range from simple stoichiometric phases such as SiO_2, to very complicated phases such as gases, slags, mattes and aqueous solutions which may involve many chemical components.

The most recent major development is an Assessment module which allows users to assess critically experimental information for a given system and obtain a set of coefficients representing the variation of thermodynamic data with temperature, composition and pressure. The Assessment module is closely integrated with the other functions of MTDATA and provides a suite of graphical tools to allow the assessor to monitor progress and to control the assessment.

It is also very easy for users to also write their own software to interact with MTDATA through its application programming interface. In this way users can set up phase equilibrium calculations and process their results directly from within their own or other commercial software. Calculations can be tailored to specific industrial applications in this way either by customising output or by using equilibrium calculations as part of a non-equilibrium process model.

S4

The Thermodynamic Database MALT for Windows

Harumi Yokokawa1), Shigeru Yamauchi2), Takafumi Matsumoto3)

1) National Institute for Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305-8565, Japan
2) National Rehabilitation Center for Disabled, Namiki 4-1, Tokorozawa, Saitama, Japan
3) Kagaku Gijutsu sha, Yushima 1-5-31, Bunkyo-ku, Tokyo 113-0034, Japan

The new version of the thermodynamic database MALT for Windows will be demonstrated. This is written using Delphi. The message language can be selected between English and Japanese.

MSI Workplace, Access to Materials Chemistry Data and Knowledge

With the Materials Science International Workplace a concept is realized that leads from basic bibliographic information to ongoing topical research projects. The initial motivation was to get the never ending flood of data and details for alloy systems organized and accessible; to set up a lasting infrastructure for this purpose.
The experience of 14 years ternary evaluation program shows that this is possible if (a) many scientists in the field share this motivation, (b) the scope extends to all materials systems and (c) past findings and ongoing works are integrated. Some 3000 new publications every year, increasing by a factor of 1.3, make such an approach mandatory.

The goal is achieved and the MSI Workplace is established.

The MSI Workplace consists from an Internet based communication platform and a PC-based application software. The main components realized in this concept are:

Data Bases, full of factual information
MSIT-Connect, an interface software to view data and documents
Science Forum, the communication platform for ongoing work and discussions,
Services, for update of data, upgrade of software, etc.

The Workplace provides access to present, past and future experimental data, as published or evaluated. In scope it covers all metal systems, the expansion into non-metal systems started with the publication year 1996.
From the data bases of the MSIT World Library documents can be compiled into the Personal Knowledge Bases where they can be handled in interactive work sessions.

The *Data Bases of the MSIT World Library* grow rapidly and contain at present :

* some 100 000 relevant links to literature, starting with the year 1900
* extended summaries of contents from all world literature on all metal systems, published since 1990.
* critical evaluations of all literature available, for some 3000 selected ternary systems.

MSIT- Connect is a PC-based handling software which in one stop allows to search, find and select by element combination the available information and to work interactively with the resulting documents.

The *Science Forum* contains 4 Info Channels, Global Workshops, the Open Internet Evaluation Program for Ternary Systems, and more. It offers the infrastructure for collaborative projects, which are open to individuals or organizations that want to join forces with MSIT, timely limited or ongoing, coordinated but free from administrative constrains.

The presentation high-lights the concept and possibilities that the MSI Workplace can offer. It demonstrates (a) MSIT Connect as an interface to the MSIT-World Library and shows (b) the interactive work with contents of the Personal Knowledge Base.

Guenter Effenberg,
Materials Science International Services, Postfach 800749, D-70507 Stuttgart, Germany

S6

Thermodynamic databases of the Glushko Thermocenter of RAS

Vladimir S. Iorish and Vladimir S. Yungman

Glushko Thermocenter of Russian Academy of Sciences, "IVTAN" Association of RAS,
HEDRC, Izhorskaya 13/19, Moscow 127412, Russian Federation

Three directions of the recent development of thermodynamic databases at the Glushko Thermocenter of RAS (GTCRAS) are described. The first direction is connected with further enhancement and updating of **IVTANTHERMO** data bank and improving of its software for thermodynamic modelling. The second direction is the development of problem-oriented datasets for various purposes connected with education and industry. The third direction is computerization of multivolume reference book **"Thermal Constants of Substances"**.

The data bank **IVTANTHERMO** contains now about 3000 tables including the properties of zinc, cupper, iron, cobalt, and nickel compounds. Besides the databases, the new **IVTANTHERMO for Windows** software provides some useful tools for database management, chemical equilibrium and heat balance calculations, data analysis, and so on.

Along with publication of the reference books, GTCRAS produces so-called problem-oriented databases:

- **IDEAL GAS** database on the thermodynamic properties of organic compounds which contains about 2000 tables.
- **DIOXINS** database consists of 424 tables for all the isomers of these compounds in gaseous, liquid and solid states.
- **THERMEL** database for thermodynamic properties of all elements of Periodic Table.
- **HTEQUIDATA** database on high temperature equilibrium data.
- **U-O** database. This database is a collection of thermodynamic property data for 23 species calculated in a wide temperature range up to 12,000K.

Computerized form of the reference book **"Thermal Constants of Substances"** (10 volumes totaling 6554 pages) presents sets of critically selected and self-consistent thermal constants for 26,976 compounds. The comprehensive bibliography amounts to more than 51,500 references.

S7

Implementing thermodynamic assessment of phase diagrams with Computational Thermodynamics Library, TDLIB'99.

E.B. Rudnyi

Chemistry Department, Moscow State University, 119899 Moscow, Russia
rudnyi@comp.chem.msu.su, http://www.chem.msu.su/~rudnyi/

Computational thermodynamics library, TDLIB'99, aimed toward thermodynamic assessment of phase diagrams is demonstrated. It includes three parts, PHASE -framework for modeling the Gibbs energy of multi-component solutions, TD_ALGO - thermodynamic algorithms, and VARCOMP2 - simultaneous thermodynamic assessment.

The library TDLIB'99 is distributed as the source code in C++ under the GNU Library Public License. The library is written under the object-oriented programming approach and it satisfies to next criteria: 1) a user is able to add new user-defined solution models to the library, 2) when the user programs the new solution model, nothing (not a line) is changed in the previously written code, 3) optimization and thermodynamic algorithms are generic and do not depend on a particular phase model.

For non-programmers, there is a compiled program for Windows 9x and Windows NT, assess.exe, which can handle a variety of thermodynamic optimization tasks.

TDLIB'99 implements a new approach that allow us to switch from "manual" to "automatic" optimization during the thermodynamic assessment. As a result one can reach success during the optimization with just rough initial estimates of unknown parameters in the Gibbs energy, even those for which some phase equilibria are not computed.

The current release of the library allows the user to employ the generalized polynomial model, including asymmetric projections of binaries, the generalized association model, and some special cases of the lattice model as a solution models for a multicomponent solution.

The work with the library is demonstrated with several examples in the area of thermodynamic assessment (the binary systems of Ba-Cu, Cu-Y, Hg-Te, Bi-Se, thermodynamics of calcium aluminates, the phase equilibria among YBa2Cu3O6+z, YBa2Cu4O8 and Y2Ba4Cu7O14+w.

The external format for all the library objects is based on the Standard Generalized Markup Language. The format is based on thermodynamic notation and self-descriptive. The format, as the library, is extendible, and if one develops new objects, he/she can naturally add them to the existing files while maintaining the backward compatibility.

With the library, there is a database with thermodynamic properties of several dozens of solid and liquid phases in the Y-Ba-Cu-O system and related substances assessed at our laboratory.

Poster Presentations A
A 1 – A 90

Non-contact Thermophysical Property Measurements of Liquid Metals

I. Egry, G. Lohöfer, S. Schneider
Institut für Raumsimulation
Deutsches Zentrum für Luft- und Raumfahrt, D-51170 Köln, Germany

In this review we shall discuss how non-contact techniques can be used for the precise measurement of thermodynamic properties of high-temperature liquids, such as metallic melts. Containerless processing eliminates unwanted reactions of the sample with a substrate thereby providing a high purity environment. Positioning and melting is achieved by electromagnetic levitation, whereas the measurements are based on videometry, pyrometry and inductive methods. The detrimental side effect of the levitation field can be further reduced by performing the experiments in a microgravity environment.

Specifically, we will discuss the measurement of following properties:

- density
- viscosity
- surface tension
- electrical conductivity

We have obtained data for the pure metals Fe, Ni, Co, Au, Ag, Cu as well as for some (binary) alloys and for Si. In addition to results obtained on ground, also results from microgravity experiments will be presented.

A2

Study of dynamic surface tension of molten silicon: development of experiments and models

Enrica RICCI, Rada NOVAKOVIC, *Elisabetta ARATO and *Marco RATTO
Istituto di Chimica Fisica Applicata dei Materiali ñ CNR
Via De Marini, 6 ñ 16149 Genova (Italy)

*Dipartimento di Ingegneria Ambientale ñ Universit‡ di Genova
Via Opera Pia, 15 ñ 16145 Genova (Italy)

Silicon crystal growth technologies (Czochralski and Floating zone methods) are controlled by complex heat and mass transfer processes, which include different flow types. The most important of them are the Marangoni flow and buoyancy-driven convection. The first one is thought to be the main cause of oxygen transfer into the crystal. However, it is difficult to isolate the Marangoni effect, since buoyancy convection coexists with other flow patterns in molten silicon.

The driving force for the Marangoni flow is the surface tension gradient. The surface tension mainly depends on temperature and adsorption parameters. At present, the surface tension of molten silicon is not known accurately, and the experimental data show a significant degree of scatter. This can be attributed to the difficulties in surface tension measurements, which are mainly due to the high melting point of silicon and to its high chemical reactivity.

A theoretical model which describe transport of oxygen in the liquid metal-atmosphere systems for different fluid-dynamic conditions has been developed.

An experimental apparatus has been designed for the direct observation of surface tension at high temperatures (up to 1800 K) in dynamic conditions, i.e. by varying temperature and oxygen partial pressure as a function of time. A stainless steel UHV chamber with a C-BN furnace has been constructed, able to work from 1 atm to 10-7 mbar. Surface tension is measuered by the sessile drop technique and the main characteristics are real time surface tension acquisition with frequency up to 10 Hz and high sensitivity (0.1 %).

In this work, the experimental procedure will be presented and some model evaluations of the oxidation/deoxidation conditions of Si melt under operating conditions similar to Czochralsky method will be reported, based on a detailed thermodynamic analysis of the Si-O system coupled with the study of oxygen transport.

Dynamic surface tension measurements on molten Sn: oxidation-deoxidation transition and model validation.

Marco RATTO, Enrica RICCI*, Elisabetta ARATO
Dipartimento di Ingegneria Ambientale ñ Universit‡ di Genova
Via Opera Pia, 15 ñ 16145 Genova (Italy)

* Istituto di Chimica Fisica Applicata dei Materiali ñ CNR
Via De Marini, 6 ñ 16149 Genova (Italy)

The interactions between liquid metals and environment (vapour phase, working atmosphere or solid container) strongly depend on the properties of the liquid surface, such as surface tension. In particular, the influence of highly reactive gases (e.g. oxygen) on a large number of metallic systems involved in many technological processes have to be accurately studied and the analysis of the interplay of different mechanisms of mass transport between liquid metals and the surrounding atmosphere are of a topical interest from a scientific and a technological point of view.

For these reasons we developed a theoretical model to evaluate the interfacial transport in a liquid metal ñ oxygen systems at different oxygen partial pressures under Knudsen conditions. When we study metals able to form volatile oxides, condensation of the oxide vapours on the reactor walls can occur and the removal of oxides from above the metal surface can significantly displace the oxidation equilibrium. By considering the contribution of the molecular oxygen and volatile oxides to the oxygen flux from the surface, oxidation and deoxidation regimes have been defined. This tool could be considered an available one to control or foresee the contamination degree of liquid metals under vacuum.

In a parallel way the evolution of the gas/liquid metal interface has been studied, in a ad hoc designed high vacuum furnace, following the variation of the surface tension with time. A low porosity alumina tube heated by Pt resistors and a monocristalline sapphire crucible are used and placed inside a stainless steel high vacuum chamber. The surface tension of the liquid has been measured by the sessile drop technique and data are acquired by an automatic procedure and processed by a specific software (ASTRAView©).

In this paper the oxygen contamination conditions for a liquid tin drop has been studied under Knudsen conditions. Experimental results show a good agreement with the developed model, which allow defining the operative parameters for oxidation and deoxidation conditions. In particular experiments confirm that an oxide removal regime occurs under a partial oxygen pressure much higher than the equilibrium one.

A4

THERMOPHYSICAL PROPERTIES OF SOLID AND LIQUID COPPER

C. Cagran, A. Seifter, G. Pottlacher

Institut für Experimentalphysik, Technische Universität Graz ,
Petersgasse 16, A - 8010 Graz, Austria
pottl@iep.tu-graz.ac.at

Wire shaped copper samples of 0.5 mm diameter and 50 mm length are resistively volume heated as part of a fast capacitor discharge circuit. Time resolved measurements with sub-µs resolution of currents through the specimen were made with a pearson probe, voltages across the specimen were determined with knife-edge contacts and voltage dividers, radiance temperatures of the sample were made with an optical pyrometer and volume expansions of the wire were measured with a fast acting CCD-camera. These measurements allowed the calculation of specific heat and dependencies between enthalpy, electrical resistivity, temperature, and density of copper up into the liquid phase.

A serious drawback of all pulse-heating experiments is, that the specimen temperature is uncertain because the spectral emissivity of the liquid is unknown and methods to measure the spectral emissivity in real-time have not been available until now. This paper will also give first results on the emissivitiy of liquid copper measured by means of a high speed laser polarimeter system.

Further more thermal conductivity of liquid copper from the raw data is estimated using the WIEDEMAN-FRANZ-law, as well as thermal diffusivity for the beginning of the liquid phase. All results are presented and discussed in comparison with literature data available.

Research partially supported by FWF Grant P12775-PHY

Investigation of the System $Nd_{0,8}Ca_{0,2}Cr_{1}$-$yLiyO_3$ at the High Temperature Range.

Anikina E.L., Burmakin E.I., Zemtsov V.I.

Institute of High-Temperature Electrochemistry, Russian Academy of Science, Urals Division, Ekaterinburg, Russia.

Solid solution on the base of neodymium chromites are perspective materials for a number of high-temperature devices. Introdution the element with smaller valencees into the chromium sublattice causes the electrical conductivity enhancement, because the Cr^{4+} concentration increases.

The results of solid solutions $Nd_{0,8}Ca_{0,2}Cr_{1-y}Li_yO_3$ investigation, where $0 \le y \le 0,2$ are presented in this work. Solid solutions were synthesized from the standard oxides and carbonates by the standard ceramic technology. From X-ray data it was shown that all received samples have perovskite structure. Opened porosity decreases from 11,2% for for y=0, to 7,0% for y=0,12.

Linear thermal expansion coefficient (LTEC) is practically constant at temperature range 300-900°C and does not depends on lithium concentrations. It is equal $\sim 8,5 \cdot 10^{-6}$ K^{-1}. LTEC temperature dependencees are linear, that indicates the absence of phase transitions in the investigated temperature range. These results were confirmed by DTA measurements.

Introdution of monovalent lithium into trivalent chromium sublattice enhances the tetravalent chromium concentration. As a result, the carrier concentration rises, that leads to the electrical conductivity increasing. The sigh and the manner of EMF dependency in the temperature range 500-1000°C allow to confirm that these materials have P - type hopping conduction.

The electrical conductivity was measured in the temperature range 500-1000°C at the air atmosphere. The maximum electrical conductivity of the best samples is equal to 33 S/cm for y=0,16 (σ=12 S/cm for y=0) at 1000°C.

A6

Electrical conductivity and thermo-e.m.f. measurements for strongly aggressive liquid semiconductors.

Yu. Plevachuk and V. Sklyarchuk

Institute of Applied Physics, Ivan Franko State University,
49 General Chuprynka Str., 290044 Lviv, Ukraine

The original experimental technique for simultaneous electrical conductivity and thermo-e.m.f. measurements in a wide temperature range (up to 2000 K) under high pressures (up to 50 MPa) has been developed. A special ceramic measuring cells were designed and constructed for investigation of chemically aggressive liquid semiconductors. Different sources of errors connected with convective flows, jamming signals, systematic deviation of measuring devices and especially with diffusion of the liquid sample into the body of the ceramic are analyzed and ways of their elimination are proposed. New results for some liquid metal-chalcogen alloys in comparison with those obtained earlier illustrate advantages of the proposed method.

Determination of the Spectral Emittance in the Visible Spectral Range at High Temperatures Supported by Laser Heating

Stefan Eckhoff, Ivo Alxneit, Markus Schubnell and Hans-Rudolf Tschudi
Paul Scherrer Institute, CH-5232 Villigen-PSI, Switzerland

The spectral emittance of hot surfaces is a crucial input for precise pyrometric temperature measurements and it is an important design parameter for choosing well suited materials in high temperature technology. With regard to current applications in high temperature solar technology ceramic materials such as Al_2O_3, ZrO_2, ZnO and Fe_2O_3 are of particular interest. However, the emittance of many of these materials is known only at moderate temperatures or at high temperatures for some discrete wavelengths merely. Moreover, for some materials, the emittances can vary strongly with temperature due to phase transitions, thermochemical reactions and, in the case of semiconductors, due to drastic changes of the Fermi-function near the bandgap. Thus, our aim was to develop an instrument to determine the spectral emittance of condensed samples at various temperatures up to 2000 K in the visible spectral range.

In the setup presented, the emittance is determined indirectly by measuring the directional hemispherical reflectance, i.e. the white probe light is focused from a particular direction onto the sample surface, whereas the reflected light is averaged over the hemisphere above. Provided that the samples are opaque, the reflectance is simply related to the emittance by Kirchhoff's law: $\varepsilon(\lambda,T) = 1-\rho(\lambda,T)$. Hence, the value derived is the directional spectral emittance in the direction of the white probe light. Since the samples (∅ = 8 mm) consist of slightly pressed and sintered powders, they have diffusely reflecting surfaces. And if these sample surfaces are assumed to be Lambertian, the directional emittance is equal to the hemispherical emittance.

With the apparatus presented the reflectance is obtained by comparing the optical response from the sample with the response of a calibrated reference. The reflected light is collected by an integrating sphere, dispersed in a spectrograph and detected by a CCD camera. The sample can be preheated up to about 1000 K by a small resistance heater right underneath the sample. In order to reach higher temperatures, a pulsed laser is focused onto the sample surface. To avoid laser induced plasma generation or oxidation in air, the integrating sphere is placed inside a vacuum chamber, which also allows measurements under controlled atmosphere. Since the apparatus is calibrated to an absolute scale, the temperature of the hot sample can be obtained by fitting the data of the thermally emitted light with Planck's radiation formula. The quality of the data is limited by the short acquisition times due to the short laser pulses.

A8

Thermal expansion of mullite

H. Schneider*, F. Frey**, G. Grunauer**

* Institut für Werkstoff-Forschung, Deutsches Zentrum für Luft- und Raumfahrt (DLR),
51147 Köln

** Institut für Kristallographie und Angewandte Mineralogie, Universität München,
80333 München

The low thermal expansion coefficient is one of the outstanding properties of mullite, characterizing it hereby as a most important constitutent of ceramics. In order to distinguish in mullite ceramics between the influence of microstructure (grain size distribution, texturing, coexisting crystalline and non-crystalline phases, pore distribution) and of crystallographic thermal expansion, mullite high temperature expansion data are highly required. For that purpose in-situ diffraction studies on undoped and on Cr-doped mullite has been performed up to 1400°C, using X-ray diffraction and synchrotron radiation techniques. The thermal expansion of mullite is higher parallel to the crystallographic b axis than parallel a. The structural control of mullite expansion is explained by the strong temperature-induced elongation of the relatively long and elastic M-O(D) bond, which has an angle of about 30° towards b, but about 60° towards a. Incorporation of Cr^{3+} into the mullite structure further decreases the thermal expansion. The in-situ diffraction studies yield evidence for discontinuous but reversible changes of the lattice spacings of mullite in the temperature frames of 400 to 500°C and 800 to 1000°C.

A9

VAPORIZATION AND THERMODYNAMICS OF INDIUM TELLURIDES.

ZlomanovV.P.,Tyulin V.I., Matveev V.K., Demin V.N.,Quispe Paucar G.A.

Department of Chemistry, Moscow State University, Moscow 119899, Russia

Indium tellurides may be used as IR detectors as well as luminescence sources. The optimum conditions for preparation a compound with well defined composition and structure may be obtained from P- T- x diagram, thermodynamic properties and molecular structure of the relavant phases. The P-T-x diagram of the In- Te system was constructed using mass-spectrometric, X- Ray and DTA techniques. A new method was developed for the crystal growth of incogruently melting In_4Te_3. The composition at maximum melting point of InTe was found as 50.5± 0.1 at% Te. The In_4Te_3 , In_2Te_3 , In_2Te_5 tellurides vaporize incongruently. The enthalpy of the reaction $In_2Te_3{}^s = 2 InTe^s + 1/2\ Te_2{}^v$ is $\Delta_r H_{298}{}^0(II) = 168.07 \pm 8.12$ kJ/mole, $\Delta_r H_{298}{}^0$ $(III) = 179.66 \pm 4.48$ kJ/mole. Below the maximum sublimation point 780 K InTe was found to vaporize congruently. The standart formation enthalpies of solid indium tellurides have been determined by direct synthesis in a calorimetric bombs.

There are only limited data on thermodynamics of gaseous molecules in the In- Te system. The molecular constants (geometry, vibration frequences of the InTe, In_2Te, $InTe_2$, In_2 Te_2 ,Te_2 molecules) have been calculated using the extended model of Badjer [1,2] . These data were used to evaluate thermodynamics of gaseous reactions in the In- Te system. The calculated constants of gaseous reactions are in good agreement with the results of mass-spectrometric study. The atomization energies are 13.9kJ/mol, 225 kJ/mol , 185kJ/mol, 344.9kJ/mol, 380kJ/mol, 623 kJ/mol for In_2, Te_2, InTe, In_2Te, $InTe_2$, In_2 Te_2 respectively.

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A10

Dilute Activity Coefficients and Solubility in Binary Oxides by Mass Spectrometry: the NaO-Al_2O_3 and MgO-Al_2O_3 Systems

A. Petric, Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L894L7
C. Chatillon, LTPCM/ENSEEG - CNRS (UMR 5614 INPG/UJF), BP.75 38402 Saint Martin d'Hères - France

Thermodynamic properties of dilute solutions of MgO and Na_2O in Al_2O_3 govern the performance of technical pure alumina parts when used in furnaces working either under inert gas or vacuum, since the volatilisation of these additives or impurities may affect both the mechanical properties of the alumina, and also the atmospheric composition which may be more or less fixed by the partial pressures of these impurities. Dilute solutions of MgO - 1000 to 100 ppm and of Na_2O - 1000 to 10 ppm - in Al_2O_3 were studied by Multiple Knudsen Cell Mass Spectrometry. Activities were deduced from the observations of the two main vaporization reactions, MgO (s.s. in Al_2O_3) $\leftrightarrow$ Mg(g) + 1/2 O_2 (g), Na_2O (s.s. in Al_2O_3) $\leftrightarrow$ 2Na (g) + 1/2O_2 (g) referred in practice to activities in the two-phase Spinel-Al_2O_3 and β alumina-$Al_2O_3(\alpha)$ domains. The main difficulty with these mixtures is determining the exact composition, especially for Na_2O since this oxide is always present in pure alumina as an impurity with a concentration of around 100 ppm, the limit of usual chemical analysis.

Preliminary special vaporization runs were performed by mass spectrometry to enable the elimination of Na_2O from Al_2O_3, before mixing the starting components (α + β). The change of activity of MgO or Na_2O as a function of composition was then used to determine the solubility limit. For MgO, our determination is slightly higher than preceeding ones while for Na_2O, our determination, shown in figure 1 is the first one. The relatively high value, ≈ 1 mol% at 1100 K, is quite unusual on the basis of ionic radius for ceramics.

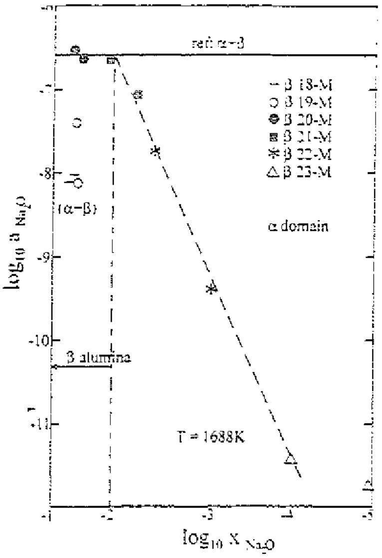

Fig. 1: Exemple of activity measurements of Na_2O in Al_2O_3(a) solid solutions.

Supersonic expansion mass spectrometric measurements on a liquid aluminum bath.

Marc Bertherat, Elisabeth Blanquet, Christian Chatillon, Michel Allibert.

Laboratoire de Thermodynamique et Physico Chimie Métallurgiques.
ENSEEG - BP 75 - 38402 Saint Martin d'Hères - France.

A mass spectrometric analyzer was built to analyze condensable and incondensable gases, extracted from liquid aluminum alloys by gas bubbling, by using of supersonic expansion. The assembly formed by the primary and secondary expansion chambers, the mass spectrometer and the gas collector is movable to be brought to the liquid metal. The gas collector and the expansion nozzle are heated to about 700°C to avoid condensation of volatile species such as Mg, Na or aluminum chloride. The respective position of the expansion nozzle and the skimmer nozzle is adjustable (x,y,z) for tuning at high temperature. The mass segregation due to supersonic expansion was found more important at high temperature than at room temperature, up to the point where hydrogen analysis in argon became insensitive. It was necessary to lower the expansion zone temperature to about 200°C to keep measuring hydrogen content in argon. Under these conditions the hydrogen content was measured with an accuracy of +-0.1%. Sensitivity for condensable species was tested on pure zinc vaporization. It was found equal to 10ppm in argon and the measured vaporization enthalpy was found equal to 100KJ instead of the 120KJ accepted in literature.

The main technical features of this apparatus, built to be used in industrial environment, will also be presented.

A 12

EQUILIBRIUM VAPORIZATION BEHAVIOR OF AIIBVI AND DISSOCIATION ENERGIES OF AIIBVI MOLECULES

(oxides and chalcogenides of the elements of zinc subgroup).

A.V.Gusarov
Glushko Thermocenter of RAS, 13/19 Izhorskaya St.,
127412 Moscow, RUSSIA
A.V.Makarov and N.V.Bagaratyan
Department of Chemistry, Moscow State University,
119899 Moscow, RUSSIA

The equilibrium vaporization behavior of five AIIBVI-compounds (ZnO - ZnTe and CdTe) has been studied by means of high temperature mass spectromerty. The measurements were carried out at temperatures up to the values, corresponding to total pressures near .1E-03 atm, it is near the limit of Knudsen conditions, for to detect the species of very low abundance. The mass spectrometers used were employed at the resolving power of near 1:1000, sufficient for detecting such species separately from the background intensities.

In all cases except ZnSe the measurements have led to detection of shutterable (near 100%) intensities for ions corresponding to diatomic molecules of AIIBVI-type. However, the detected signals were near the limit of apparatus sensitivity; so the reliable isotopic confirmation of chemical nature for the molecules detected has not been fulfilled. The detected signals have been treated as referring to upper limits of corresponding vapor pressures (near .nE-09 atm). For ZnSe the corresponding signals were not detected, that lead to upper limit of vapor pressure near .1E-09 atm.

The obtained values correspond to upper limits of dissociation energies: 199, 174, 128, 86 and 61 KJ/mole, for ZnO - ZnTe and CdTe, respectively (T=0 K). The measurements show, that the majority of the early high temperature mass spectrometric investigations, leading to higher values, are erroneous.

HIGH TEMPERATURE MASS SPECTROMETRIC STUDY OF THERMODYNAMIC PROPERTIES AND VAPORIZATION PROCESSES IN THE Al_2O_3-SiO_2 SYSTEM

S.I. Shornikov, I.Yu. Archakov

Institute of Silicate Chemistry of the Russian Academy of Sciences,
ul. Odoevskogo 24, korp. 2, 199155, Saint Petersburg, Russia

Due to the specially designed high temperature ion source with the number of unique characteristics the vaporization processes and thermodynamic properties of the Al_2O_3-SiO_2 system melts were investigated in the temperature range 1720-2520 K by mass spectrometric Knudsen effusion method.

The mass spectra of vapor over the melts of Al_2O_3-SiO_2 system was reported in our previous studies [1]. The observed vapor species showed that the main evaporation processes of Al_2O_3-SiO_2 system melts are the same as in the case of individual oxides.

The difference in the observed evaporation rates of system components corresponding to the individual oxides (Al_2O_3 and SiO_2) caused the changes in the condensed phase sample composition from initial (incongruent evaporation). This fact gives an opportunity to investigate the thermodynamic properties of liquid phase of studied system using the approaches based on the Gibbs-Duhem equation. Nevertheless the composition corresponding to the liquidus line point is characterized by the constant relation of the evaporation rates due to the constant activities of the condensed phase components (congruent evaporation). The calculations of the compositions of such points using Herts-Knudsen equation permitted to estimate the liquidus line points placements and to use these data as the limits in the Gibbs-Duhem integration procedure. As a result of these observations the congruent character of mullite melting at 2180±10 K was shown. The activities of Al_2O_3 and SiO_2 in the liquid phase of Al_2O_3-SiO_2 system were obtained. The partial and integral enthalpies and entropies in the studied system were calculated using this data. The combination of thermodynamic information corresponding to liquid and solid phases of Al_2O_3-SiO_2 system permitted to evaluate the fusion enthalpies of the system.

The present study was carried out with the financial support of Russian Fund of Basic Researches (RFBR, grant N 98-03-32630a).

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HIGH TEMPERATURE STUDY OF THE EVAPORATION OF SILICON MONOXIDE

S.I. Shornikov, I.Yu. Archakov

Institute of Silicate Chemistry of the Russian Academy of Sciences,
ul. Odoevskogo 24, korp. 2, 199155, Saint Petersburg, Russia

The processes of the evaporation and the thermodynamic properties of silicon monoxide in comparison with $Si+SiO_2$ equimolar mixture were studied by the high temperature mass spectrometric Knudsen effusion method at 1200-1550 K. The investigations were carried out using MI 1201 mass spectrometer with molybdenum effusion cells with the different ratios of effusion and evaporation squares.

The consideration of the mass spectra at low ionizing energies indicated the presence of (SiO) and (Si_2O_2) vapor species over the studied samples. The determined values of the appearance energies of corresponding ions were the same as in the previous studies of the SiO_2 evaporation.

The obtained values of the partial evaporation coefficients for the silicon monoxide were close to the same in the case of silicon dioxide evaporation [1] and significantly differs from the $Si+SiO_2$ equimolar mixture case. This difference could be the criteria of the identification of these two similar processes (SiO and $Si+SiO_2$ equimolar mixture evaporation) taking into account the same vapor composition and the coincide values of the equilibrium partial pressures of the vapor species.

The present study was carried out with the financial support of Russian Fund of Basic Researches (RFBR, grant N 98-03-32630a).

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A 15

MASS SPECTROMETRIC STUDY OF VAPORIZATION OF LANTHANIDE TRICHLORIDES AND THERMODYNAMIC PROPERTIES OF GASEOUS MOLECULES AND IONS

L.S. Kudin, A.M. Pogrebnoi, I.V. Khasanshin, V.B. Motalov

Department of Physics, State University of Chemical Sciences and Technology,
Prosp. Engelsa 7, 153460 Ivanovo, Russia

The results of Knudsen cell mass spectrometric thermodynamic study of lanthanum, neodymium, gadolinium, terbium, dysprosium, holmium, thulium, ytterbium, and lutetium trichlorides vaporisation are presented. In contrast to preceding investigations in the temperature range between 800 and 1300 K various neutral and charged associated species were identified in saturated vapours for the first time. The dimer molecules, Ln_2Cl_6, have been registered for all trichlorides. Extremely high association degree has been observed for thulium and lutetium trichloride, in particular, the molecules and ions as large as $(TmCl_3)_5$, $Cl^-(TmCl_3)_8$, and $(LuCl_3)_6$, $Cl^-(LuCl_3)_6(LuCl_3)_6$ have been discovered. As it follows from thermodynamic calculations, the mole fraction of dimer molecules increases with temperature increase reaching its maximum when a temperature approaches to a boiling point and amounts to 10 - 60 per cent depending on lanthanide. At temperatures above the boiling point a thermodynamic stability of dimers decreases since the Gibbs free energy of the process $Ln_2Cl_6 \rightarrow 2LnCl_3$ becomes negative. For more complex molecules calculations predict quite low mole fractions, not exceeding 1 per cent, given the larger is the size of the molecules, the lower is their mole fraction in the vapour.

All the charged associated species can be considered as products of interaction of Cl^-, Ln^+ and $LnCl^+$ ions with neutral molecules at the surface layer. A such mechanism of formation of ions permits to interpret a correlation between the association efficiencies for neutral molecules and ions. The molecular and charged associated species are stable enough thermodynamically and may exist in saturated vapour at temperatures that are much higher than those achieved in our experiments. An analysis of the Gibbs free energy changes for a variety of decay processes of complex molecules and ions has demonstrated that the most probable decay channel is a detachment of the dimer molecule.

A comparative analysis of thermodynamic characteristics (sublimation and formation enthalpies, atomisation and dissociation energies, electron affinity etc.) of gaseous molecules and ions along the lanthanide series is given.

A16

MASS SPECTROMETRIC STUDY OF THE MOLECULAR AND IONIC SUBLIMATION OF ALKALI HALIDE SINGLE CRYSTALS

M. F. Butman[1], **A. A. Smirnov**[1], **L. S. Kudin**[1], **and Z. A. Munir**[2]

1. Department of Physics, State University of Chemical Sciences and Technology, Prosp. Engelsa 7, 153460 Ivanovo, Russian Federation; 2. Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA.

A mass spectrometric method was used to study the kinetics of molecular and ionic sublimation of alkali halide single crystals - CsI, KBr, KCl, NaCl and LiF - with the purpose of establishing the chemical composition of vaporizing fluxes and clarifying the vaporization rate-controlling factors and the mechanisms of surface association reactions.

From the analysis of the electron-impact-ionization mass spectra it is shown that all these salts vaporize to give monomer and dimer molecules. In the case of LiF an appreciable fraction of trimers is found. A departure of the temperature dependencies of ion currents from linearity typical in the Knudsen cell measurements provides the temperature dependence of the vaporization coefficient of both monomers and dimers due to the combined effect of the factors related to surface structure roughening, impurity segregation, and electric boundary layer. The dimer-to-monomer ratio is found to increase with the temperature at a continually increasing rate in the LiF and NaCl cases. In the KCl, KBr, and CsI cases this rate passes through a maximum. It is observed that the electron-impact-fragmentation pattern of MX molecules (M is the alkali atom, X is the halogen) is temperature-dependent, in the CsI, KCl, and KBr cases this pattern reproducibly passes through a minimum. It is concluded that molecules desorbing from an open crystal surface may possess excessive vibrational and rotational energy compared to that characteristic of thermal excitation.

In the thermionic emission mass spectra, M^+, M_2X^+, $M_3X_2^+$ and M_2^+ positive ions and X^- and MX_2^- negative ions were identified, the emission of negative ions was much weaker. It is found that in contrast to the molecular sublimation the compositions of ion beams from the Knudsen cell and from the free crystal surface differ significantly. The temperature dependence $\ln I(M^+) - 1/T$ reveals a change in slope in KCl and CsI cases, whereas it passes successively through a maximum and a minimum with a temperature increase in the NaCl and KBr cases. These observations indicate that a positive intrinsic surface charge exists in the former cases and a negative one exists in the latter cases. Based on these results, a novel method of determining the vacancy formation energies is proposed. The probable mechanisms of ion-molecule reactions are considered.

The results are discussed in light of the terrace-ledge-kink and surface charge models.

Synthesis and investigation of the properties of gaseous high transition metal fluorides

J. V. Rau, **N. S. Chilingarov, L. N. Sidorov**
Chemistry department, Moscow State University, 119899 Moscow, Russia,
e-mail: jrau@phys.chem.msu.ru
S. Nunziante-Cesaro, G. Balducci
Chemistry department, University of Rome, I-00185 Piazzale Aldo Moro, Rome, Italy,
e-mail: balducci@axcasp.caspur.it
L. Bencze*, A. Popovic
J. Stefan Institute, SLO - 61111, Jamova 39, Ljubljana, Slovenia
**On leave from Eotvos University, Dept. Phys. Chem., H-1117, Budapest, Pazmany P. setany 2, Hungary,*
e-mail: bencze@ludens.elte.hu

A considerable advance in the synthesis of high transition metal fluorides - compounds having an unusually high degree of oxidation of the metal - has been made recently. The properties of these new compounds are of scientific interest, however their synthesis and investigation are hampered by their thermodynamic instability. Knudsen effusion mass spectrometry has been applied to study solid-phase reactions of fluorination in the CoF_3(s) - TbF_4(s) and MnF_3(s) - TbF_4(s) systems. The gas phase composition in these systems has been studied at different temperatures and concentration of the fluorinating agent in the initial mixture. As a strong fluorinating agent TbF_4(s) has been used for solid-phase synthesis in situ. It has been proved that atomic fluorine is released during TbF_4(s) thermal decomposition in the temperature range 600 – 700 K and therefore fluorine atoms play an important role in the fluorination reaction. In mass spectrometric experiments the optimal synthesis conditions have been found to obtain information on the hyperfluorinated gaseous species CoF_4 and MnF_4. The very same synthesis in situ procedure was utilized to investigate cobalt and manganese tetrafluoride by employing FTIR spectroscopy coupled with the matrix isolation technique. The infrared spectra of argon isolated CoF_4 and MnF_4 molecules have been determined and the metal-fluorine stretching mode has been assigned. The possibility to produce FeF_4 in the gas phase over the FeF_3(s) - TbF_4(s) system has been considered.

A18

The investigation of fluorination of $CoF_2(s)$ and $CoF_2(s)$ - $TbF_3(s)$ mixture by atomic fluorine

N. S. Chilingarov, J. V. Rau, M. S. Leskiv, S. V. Abramov, A.V. Kepman,
and L. N. Sidorov
Chemistry department, Moscow State University, 119899 Moscow, Russia,
e-mail: nsc@phys.chem.msu.ru

The atomic fluorine interaction with CoF_2 results in the CoF_4(gas) formation at $P(F) = 10^{-5} - 10^{-4}$ atm and $T = 600 - 800$ K. As this takes place, cobalt tetrafluoride is the only fluorination product at $T < 650$ K. The investigation of solid-phase fluorination in the $CoF_3(s)$ - $TbF_4(s)$ system under the excess of TbF_4 demonstrates that in the temperature range 620 - 700 K only CoF_4 molecules sublimate into the gas phase, while CoF_3 sublimation does not take place.

In this research the gas phase composition of $CoF_2(s)$ - F and $CoF_2(s)$ - $TbF_3(s)$ - F systems has been determined in the temperature range 650 - 850 K and different initial compositions of the $CoF_2(s)$ and $TbF_3(s)$ mixture. The role of TbF_3 in the CoF_4(gas) synthesis has been investigated.

The equipment employed for fluorination consisted of a nickel tube with two independently heated zones: an atomic fluorine generator and a reactor. Molecular fluorine entered in the generator from an external reservoir. The partial heterogeneous dissociation took place in the generator at ~1000 K. Fluorine atoms from the generator entered the reactor and interacted with the sample. The gas phase components passed into the ion source of the mass spectrometer through the effusion orifice (d = 0.3 mm) and were mass analyzed. The calculation of the partial pressures of the gas phase components was based on measured ion intensities.

The fluorination has been executed at specified values of F_2 admission inlet, and temperatures of generator and reactor. The role of TbF_3 in the formation of CoF_4(gas) has been studied by comparative analysis of the results obtained during the investigation of the fluorination process in the $CoF_2(s)$ - $TbF_3(s)$ system, that had different amount of TbF_3 (from 0 to 90 mol%). The search of equilibrium conditions in the reactions with cobalt fluorides participation has been carried out in $CoF_2(s)$ - F system at 750 - 850 K.

A 19

Thermodynamics of Liquid Silicates.

B.M.Mogutnov, A.I.Zaitsev, N.E.Shelkova and A.D.Litvina
Institute for Metal Physics and Functional Materials, I.P.Bardin Central Research Institute for Ferrous Metallurgy
9/23 2-nd Baumanskaya Ul., Moscow 107005, Russia

The paper generalises the results of the recent thermodynamic studies of liquid silicates in the systems of various nature and complexities: Na2O-SiO2, K2O-SiO2, CaO-SiO2, MnO-SiO2, CaF2-CaO-SiO2, CaO-Al2O3-SiO2, CaF2-CaO-Al2O3-SiO2. Knudsen effusion mass spectrometry and the method based on generation in the effusion cell of reduction or exchange reactions producing volatile substances were used. Representative files of experimental data on activities of all components in wide temperature and concentration ranges were obtained for each system. One of the principal results of these studies is that the entropy of the liquid solutions observed in experiment is substantially lower than the configuration entropy expected from the widely spread ionic concept of molten silicate structure. It is even lower than the configuration entropy characteristic to the ideal molecular solutions. These facts mean that the real number of particles in the in molten silicates is well below that of ions and even below the number of molecules. Accordingly it was assumed that strong interaction between molecules of the components results in formation of molecular complexes and Prigogine's theory of associated solutions was used to develop a model of liquid silicates. The melts were supposed to consist of molecules, heteromolecular associates (2CaO(Al2O3, CaO(SiO2, CaO(Al2O3(2SiO2, etc) and SiO2 networks of various configurations and size. The thermodynamic description of a multicomponent system included descriptions of all simpler constituents and all associates inherent in the simpler constituents were supposed to exist in the more complex solutions. The least-squares treatment of the experimental data revealed that the suggested model describes, with a precision not worse than the experimental one (1 - 3 %), the thermodynamic functions of not only molten silicates, but of liquid solutions of inorganic compounds in general. In complete agreement with the laws of chemical equilibria, the thermodynamic characteristics of the same association reaction do not depend on the composition. Further evidence of correctness of the associated-solution model was obtained by calculation of phase diagrams, which included extrapolation of the components activities to unstudied temperature and concentration ranges. Finally, it was shown that the associated-solution model allows qualitative treatment of the liquid(glass transformations and explanation of experimental data on the structure and properties of silicate melts.

A 20

Thermodynamic properties and phase equilibria in Na2O-SiO2 and K2O-SiO2 System

A.A.Tsaplin, A.I.Zaitsev, N.E.Shelkova and B.M.Mogutnov
Institute for Metal Physics and Functional Materials, I.P.Bardin Central Research Institute for Ferrous Metallurgy
9/23 2-nd Baumanskaya Ul., Moscow 107005, Russia

Knudsen effusion mass spectrometry and the method based on generation in the effusion cell of reduction reactions producing volatile suboxides were used to study the thermodynamic properties of the Na2O-SiO2 and K2O-SiO2 systems in solid and liquid states. Nb, Ta, Mo or Ni served as reductants. Me+, Me2O+, MeO+, O2+, MO+, MO2+ (M=Nb, Ta, Mo; Me=Na, K), MoO3+ and NiO+ were detected in the mass spectra of the saturated vapour. Me, TaO2, NbO2, MoO2, NiO and MeO2 were found to be the main vapour species and their partial vapour pressures were measured and used for calculation of a (Me2O). The activity of SiO2 was calculated using the Gibbs-Duhem equation. The Gibbs energies of formation of solid sodium and potassium silicates from solid K2O, (-Na2O and quartz were approximated using the following equations (in J mol-1): (fG(3Na2O(8SiO2) =-(641300(8300)((73.7(7.7)T, (fG(Na2O(2SiO2)=((220980(2150)((17.1(2.1)T, (fG(Na2O(SiO2)=((230800(1200)+(4.6(1.2)T, (fG(3Na2O(2SiO2)=((552500(3000)((30.75 (2.75)T, (fG(2Na2O(SiO2)=-(381300(1900)+(20.7(1.8)T, (fG(K2O(4SiO2)=-(324500(2600)-(5.9(2.1)T, (fG(K2O(2SiO2)=-(337700(1700)+(10.4(1.5)T, (fG(K2O(SiO2)=-(291900(1200)+(10.5(1.2)T. The thermodynamic functions of the liquid solution were described by the associated-solution model under the assumption that binary associates and SiO2 polymer complexes exist in the melts. The model and the thermodynamic functions of solid compounds were applied for the computation of the phase diagram. The computed co-ordinates of the invariant points and the miscibility gap are shown to agree with the available experimental data.

High-Temperature Mass Spectrometric Studies of Metallic Alloys and Mixtures of Inorganic Compounds

A.I.Zaitsev
Institute for Metal Physics and Functional Materials, I.P.Bardin Central Research Institute for Ferrous Metallurgy
9/23 2-nd Baumanskaya Ul., Moscow 107005, Russia

This paper is concerned with high-temperature thermodynamic research of systems of various complexity formed by metals, non-metal and inorganic compounds. Knudsen mass spectrometry was chosen as a basic method because it allows simultaneous determination of partial thermodynamic characteristics of the majority if not all of the components in a multicomponent system in one experiment. In order to overcome the disadvantage, the relative character of vapour pressure measurements, inherent in this technique, double-cell effusion blocks were used, one cell being filled with a reference substance. Using of these type blocks assisted in some cases in assignment of overlapping mass spectra lines. Another way to eliminate this disadvantage consisted in simultaneous measuring the ionic intensities of representative ionic species at different temperatures and molar fractions. Complete information on the composition of the saturated vapour and partial pressures of its species was obtained in each experiment so that it was possible to calculate activity of the same component in several (up to 4 or 5) independent methods. A new experimental approach to the Knudsen mass spectrometry of condensed matter with low vapour pressure was developed. The impossibility to obtain measurable vapour pressures in convenient temperature range was overcome by initiating reactions, which produced volatile substances. With this purpose molybdenum, niobium, or calcium fluoride were added to the samples. The first two reduced the oxide components to gaseous suboxides, the third started the exchange reactions resulting in formation of gaseous fluorides. This method complicated the mass spectra, but in any case molecular precursors of each ion and corresponding contributions to ionic intensities could be determined through side experiments and thermodynamic calculations of gaseous equilibria. Two types of isothermal-evaporation experiments have been devised to prove decisively that the state of equilibrium existed in the effusion cell. In the first, the mixtures of the same initial composition were evaporated from effusion cells of different orifice areas. In the second, melts had different initial compositions chosen in such a way that their configuration points should fall on the same distillation line.

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Decomposition and Vaporization of Samarium Triiodide

L.N. Gorokhov, A.V. Gusarov, and A.M. Emelyanov
Glushko Thermocenter of RAS, 13/19 Izhorskaya st., 127412 Moscow, RUSSIA

Heating of samarium triiodide results in evolution of iodine and formation of the diiodide. SmI_2 molecules were detected by vaporization of pure liquid SmI_2 (C. Hirayama *et al.*, Inorg. Chemistry, 1974, Vol. 13, p. 2804). At present, there is no information in the literature on existence of SmI_3 gaseous molecules. At initial stages of decomposition process, the thermodynamic activity of SmI_3 in the SmI_3 - SmI_2 system must be high enough to enable measurements of $SmI_3(g)$ partial pressure. To prove this idea, a mass spectrometric study of vapor composition during samarium triiodide heating was carried out. Sm^+, SmI^+, SmI_2^+, SmI_3^+, I^+, and I_2^+ ions were detected in the mass spectrum at $T \approx 900$ K. The presence of SmI_2 and SmI_3 molecules in vapor, as well as I and I_2, is evident from the mass spectrum. The ratio of the ion intensities $SmI_3^+/SmI_2^+ \approx 0.1$ was found at the beginning of the experiment. After further heating at higher temperatures this ratio gradually changed to ≈ 0.0001. At $T \approx 1050$ K, $Sm_2I_3^+$ ions were detected. The neutral precursors of $Sm_2I_3^+$ ions are Sm_2I_4 molecules. The enthalpies of SmI_2 vaporization in monomeric and dimeric forms were calculated from the temperature dependence of SmI_2^+ and $Sm_2I_3^+$ ion intensities by the second- and third-law treatment of data.

This work was supported by the Russian Federation for Basic Research (RFBR Project 97-02-16847).

Vaporization and Phase Diagram Studies on Mn-Te-O system

T.S. Lakshmi Narasimhan, M. Sai Baba and R. Viswanathan
Materials Chemistry Division
Indira Gandhi Centre for Atomic Research
Kalpakkam - 603 102
Tamil Nadu, India

In continuation of our recent mass spectrometric investigations on TeO_2 and MnTe systems, a systematic vaporization thermodynamic study of Mn-Te-O ternary system was taken up. With an initial objective of studying the vaporization behavior of $MnTeO_3$, isothermal Knudsen effusion mass spectrometric experiments were conducted at T = 950 K on samples of different initial compositions along the MnO-TeO_2 pseudo binary tie-line (x MnO + (1-x) TeO_2 where x = 0.50, 0.54, 0.57, and 0.67). Te^+, Te_2^+, TeO^+, TeO_2^+, and O_2^+ were the ions observed (at ~ 40 eV) in the equilibrium vapor, with Te^+ formed solely due to fragmentation. The vaporization experiments were terminated when the ion intensities were steady for considerable time. The residues in all cases showed the presence of Mn_3TeO_6 and $MnTeO_3$. Another series of experiments were conducted by adding excess of MnO to samples with x = 0.50, 0.57, and 0.67 to make x = 0.8 in each case. These experiments were characterized by high initial evolution of Te_2(g). The residues showed the presence of Mn_3TeO_6 and Mn_3O_4 and absence of $MnTeO_3$. These results indicated that vaporization of $MnTeO_3$ might involve loss of Te and O in a ratio greater than 1:2 and that $MnTeO_3$ as well as Mn_3TeO_6 might be able to coexist with Mn_3O_4 rather than with MnO. However, no conclusive inferences could be made on the exact nature of invariant condensed phase - vapor phase equilibria. For this purpose, separate equilibration experiments were carried out at T = 950 K under static (in evacuated and sealed quartz tubes) and dynamic (flowing argon) conditions with samples consisting of mixtures of a) MnO + TeO_2, b) Mn + MnO + TeO_2, and c) $MnCO_3$ + TeO_2. On the basis of X-ray diffraction analysis of the products, the following three phase regions were identified : a) $MnTeO_3$ + Mn_3TeO_6 + $Mn_2Te_3O_8$, b) $MnTeO_3$ + Mn_3TeO_6 + Mn_3O_4, c) $MnTeO_3$ + Mn_3O_4 + $Mn_6Te_5O_{16}$, and d) MnO + Mn_3O_4 + $Mn_6Te_5O_{16}$. These results together with the available information in the literature were used to construct a ternary section of Mn-Te-O phase diagram. Mass spectrometric experiments with above three phase mixtures are underway to deduce finally thermodynamic data of the ternary phases $MnTeO_3$, Mn_3TeO_6, $Mn_2Te_3O_8$, and $Mn_6Te_5O_{16}$.

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Mass Spectrometric and Theoretical Investigations of *Ln*Cl_3(g) and Ln_2Cl_6(g)

Jan Kapała, Mirosław Miller,

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław University of Technology, Wybrzeże St. Wyspiańskiego 27, 50-370 Wrocław, Poland

and Szczepan Roszak

Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wybrzeże St. Wyspiańskiego 27, 50-370 Wrocław, Poland

Thermodynamic stability of gaseous lanthanide halides is of the great fundamental importance. The influence of the f-electrons on the valence electrons in the lanthanide atoms, and therefore on the chemistry of their compounds is very important for the understanding of nature of chemical bonding. Thermodynamic properties, as enthalpy of vaporization and enthalpy of formation should show some regularities on going from La to Lu compounds. These regularities should be understandable considering the electronic configurations of the molecules.

The vaporization of $LnCl_3$, *Ln* = Ce, Pr, Nd, Dy, was investigated in the present study by the Knudsen effusion mass spectrometry. The monomer and dimer partial pressures in the equilibrium vapor of the compounds were determined. Molecular parameters of $LnCl_3$(g) and Ln_2Cl_6(g) were determined theoretically by the H-F, MP2 and B3LYP approachs and the thermodynamic functions of these species were computed applying statistical thermodynamics. The enthalpies of sublimation of $LnCl_3$(g) were evaluated according to the second and third-law methods. A recommended values of $\Delta_{sub}H^0(298) = 334.8 \pm 7.2$ kJ mol^{-1} ($CeCl_3$), 323.3 ± 3.5 kJ mol^{-1} ($PrCl_3$), 317.3 ± 6.4 kJ mol^{-1} ($NdCl_3$), and 305.3 ± 6.3 kJ mol^{-1} ($DyCl_3$), resulted for the sublimation enthalpies of gaseous species given in brackets by compilation of the present study with the data available in literature. The enthalpies of sublimation $\Delta_{sub}H^0(298) = 443.2 \pm 12.0$ kJ mol^{-1} (Ce_2Cl_6), 418.7 ± 12.1 kJ mol^{-1} (Pr_2Cl_6), 414.8 ± 11.3 kJ mol^{-1} (Nd_2Cl_6), and 354.1 ± 11.3 kJ mol^{-1} (Dy_2Cl_6), were obtained for dimeric species by the use of the third law method.

Thermodynamic Investigation and Theoretical Calculations on $ALn\mathrm{Cl}_4$(g), A = alkali metal, Ln = lanthanide

Jan Kapala[a]*, Iwona Lisek*[a]*, S.Roszak*[b]*, and M.Miller*[a]

Institutes of [a]*Inorganic Chemistry and Metallurgy of Rare Elements and* [b]*Physical and Theoretical Chemistry, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland*

Lanthanide halides are known to form various kinds of halogen-bridged vapour complexes. Recently, the iodide and bromide systems have been systematically investigated by means of Knudsen effusion mass spectrometry because of their importance for high intensity metal halide lamps. The aim of the present work was the determination of partial pressures over the $A\mathrm{Cl}$ – $Ln\mathrm{Cl}_3$ systems, A = Na, Cs, Ln = Ce, Pr, Nd, Dy, and the evaluation of the thermodynamic stability of $ALn\mathrm{Cl}_4$(g) from the equilibrium data. Theoretical calculations of the $ALn\mathrm{Cl}_4$(g) structure were performed by the MP2 and B3LYP approachs and the nature of the bridge bonding in these molecules was discussed considering electron density changes on going from the monomer species to the bridged complexes. Thermodynamic functions of $ALn\mathrm{Cl}_4$(g) were estimated from the molecular structure parameters by use of the statistical thermodynamics. The second law and third law evaluations of the dissociation enthalpy of $ALn\mathrm{Cl}_4$(g) were performed using the experimental equilibrium pressures in addition to the thermodynamic functions of the gaseous species involved. Estimations of the chemical transport of Ln in the studied system was carried out, as well.

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Vaporisation of CsBr and Thermochemistry of the Homocomplexes $(CsBr)_n(g)$, $n = 2, 3, 4$

K. Hilpert[a]*, M.Miller*[b]*, and A.Feltrin*[c]

[a] *Research Centre Jülich, 52425 Jülich, Germany*
[b] *Wroclaw University of Technology, 50370 Wroclaw, Poland*
[c] *University Rome „la Sapienza", P. la Aldo Moro 5, Rome, Italy*

The vaporisation of CsBr(s) was investigated in the temperature range between 612 K and 895 K by Knudsen effusion mass spectrometry. The ions Cs^+, $CsBr^+$, Cs_2Br^+, $Cs_2Br_2^+$, $Cs_3Br_2^+$, and $Cs_4Br_3^+$ were detected and their appearance potentials determined. The species CsBr(g), $(CsBr)_2(g)$, $(CsBr)_3(g)$ and $(CsBr)_4(g)$ were identified in the vapour and their partial pressures determined using quantitative vaporisation.

Enthalpies and entropies of sublimation resulted according to the second-law and third-law methods. The thermochemical functions for the gaseous species used in the third law evaluation were computed by the use of statistical thermodynamics from the molecular parameters. The parameters were estimated by the F,G matrix method using the experimental data of CsBr(g) and $(CsBr)_2(g)$ from the literature. The two different structures planar ring (D_{4h} symmetry) and cubic (D_d symmetry) were considered for the tetramer species. Selected values for the standard sublimation enthalpy at 298 K were obtained for CsBr(g), $(CsBr)_2(g)$, $(CsBr)_3(g)$, and $(CsBr)_4(g)$ as: 199.9 ± 4.7 kJ mol^{-1}, 236.8 ± 5.0 kJ mol^{-1}, 280.2 ± 7.9 kJ mol^{-1}, and 251.0 ± 12.4 kJ mol^{-1}, respectively.

Neutron Powder Diffraction Studies of Phase Transformations under Effusion Conditions

Camille Jones and Jimmie G. Edwards
Department of Chemistry, University of Toledo, Toledo, Ohio USA

Neutron diffraction for the first time was used to observe phenomena in an effusion experiment. It was demonstrated that the anomalous temperature dependence of vapor pressure observed for Ga_2S_3 and $MnGa_2S_4$ during effusion experiments is a manifestation of a condensed-phase transformation. Crystal structures were determined from the neutron powder diffraction data by the Rietveld method. By their crystallographic features the observed phase changes were classified as order-disorder transformations. The results of this study are in agreement with a thermodynamic theory, which explains the anomalous vapor-pressure dependence on the basis of a condensed-phase transformation and calls for a low value for the enthalpy of transformation.

The phase transformations that are the subject of this work were discussed for many years as proposed, but unproven, reasons for the anomalous temperature dependence of vapor pressure observed in certain binary chalcogenides in the Ga-S, MnS-Ga_2S_3, and Ga-Se systems. In the case of Ga_2S_3, the anomaly is an increase in the partial pressure of $Ga_2S(g)$ in an effusion cell with decreasing temperature at 1240 - 1230 K and then a constant vapor pressure down to *ca.* 1150 K. The structural change observed by neutron diffraction was a change from α-Ga_2S_3, which is monoclinic, to a hexagonal phase above 1240 K. The ternary metal chalcogenide $MnGa_2S_4$ was also known to exhibit anomalous temperature dependence of vapor pressure in the vicinity of 1243 K more pronounced than that of α-Ga_2S_3. Neutron diffraction patterns of $MnGa_2S_4$ revealed a phase transformation to a high-temperature phase at 1245 ± 5 K.

Experimental studies were done at the IPNS spallation source at Argonne National Lab. Powder samples of 3-6 g were studied in quartz effusion cells heated in neutron beams in vanadium furnaces. Temperature programs and data collection times were based on experimental evidence and theoretical predictions in the literature to gain maximal information from scattered neutrons. Two types of scattering experiments were performed, one type with high resolution in real space to yield information on diffuse scattering, and a second type with high resolution in reciprocal space for Rietveld refinement of crystal structure. In this paper detailed results, structures, and conclusions from the experiments are presented, correlations with theoretical predictions are shown, and a new method of high temperature chemical study is suggested.

HIGH TEMPERATURE MASS SPECTROMETRIC INVESTIGATION OF SOLID ELECTROLYTES

A.M. Pogrebnoi, L.S. Kudin

Department of Physics, State University of Chemical Sciences & Technology,
Prosp. Engelsa,7, 153460 Ivanovo, Russia

The results on the thermal emission of neutral and charged species from some solid electrolytes (SE) obtained by high temperature mass spectrometric technique are summarized. The substances which have been studied are as follows: $RbAg_4I_5$, KAg_4I_5, $CsAg_4I_5$, Li_4GeO_4, Li_4SiO_4, AgI, CuI, CuCl, $Li_4TiP_2O_9$, $Na_4TiP_2O_9$, $Li_{0.03}V_2O_5$, $Li_{0.2}VO_{2.6}$, $GdCl_3$-RbCl. Various ions and molecules have been found in vapors over heated SE. It has been shown that SE may be considered effective emitters of atomic alkaline metal ions. In some cases, the vaporization accompanied by emission of cluster ions and molecules. Metastable alkaline metal cluster ions M_4^+ and M_5^+ have been discovered for the first time. Extremely low temperatures of the appearances of ions were established in some cases. Thus for MAg_4I_5, where M = Rb, K, Cs, the threshold temperatures were as low as 220-235 °C for MAg_4I_5, M = Rb, K, Cs, and 350 ° C for $GdCl_3$-RbCl system. Intense ion currents of admixed alkaline metal ions are observed usually in the thermal emission mass spectra of the positive ions, due to the traces of alkaline metal compounds in the substances. Not only the thermal emission properties but also electroconductivity of SE may be affected by these impurities. Therefor the content of alkaline metal compounds should be controlled.

A kinetic effect has been revealed in the course of the investigation of Li_4SiO_4, $RbAg_4I_5$ and $CsAg_4I_5$. At constant temperatures the ion current intensities continued to increase until maximum values were reached. Kinetic curves have been obtained and, by a standard procedure of experimental data treatment, the rate constants have been determined. The effective activation energies of diffusion of ions from a bulk into the surface layer have been calculated. The interpretation of the kinetic effect was assumed.

Through temperature dependences of ion current intensities, work functions of ions have been determined by using Richardson-Dushman equation. Inversion of work functions near the phase transition point in Li_4GeO_4 has been discovered. The values of work functions of ions for investigated substances vary from 1.2 to 6 eV.

Different ion-molecular, ion-ion, and molecular-molecular equilibria have been studied. Formation enthalpies of cluster molecules and ions have been calculated.

Pyrometric Temperature Measurements in Presence of External Radiation

H. R. Tschudi and Chr. Müller
Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

Accurate temperature information is crucial for process control in many different fields (metallurgy, semiconductor industry, chemical processing etc.). Thermally emitted radiation being one of the most convenient sources for this information, multi-wavelength pyrometry is an established technique to measure surface temperatures in the absence of external light sources. But ordinary pyrometry fails if the emittance is unknown or changing or if external light sources strongly interfere. A device based on a novel multi-wavelength analysis of the radiation emitted by a hot and illuminated Lambertian surface is presented that allows a reliable temperature measurement even in these cases.

For the separation of thermally emitted and reflected external radiation, an accurate knowledge of the spectral emittance/reflectance of the sample is required. In our procedure, this quantity is determined in situ by performing a second measurement with additional light e.g. from strong electric flash. The strength of the flash and the relative spectrum of the interfering external radiation are probed with a cooled Lambertian reflectance reference near the sample. In a first step, the spectral reflectance of the sample is determined from spectra recorded with and without flash. The temperature and the total incoming irradiance are then obtained from a least-square fit of the input spectra with an analytical model of the emitted thermal plus the superimposed reflected external radiation. The method delivers also estimates for the statistical accuracy of the measured temperature and irradiance values. It causes no problem to measure temperatures through a quartz window or a mirror of sufficient optical quality and effects of absorbing gases or vapours may be minimized by an appropriate choice of the spectral intervals used for the analysis.

As an illustration, temperature measurements are presented performed on the TREMPER reactor at the solar furnace of the Paul Scherrer Institute. Small pellets ($\emptyset \approx 8\,\mathrm{mm}$) of slightly compressed powders are exposed to concentrated solar radiation (maximal flux $\approx 3\,\mathrm{MW\,m^{-2}}$) on a cooled sample holder. The sample is placed inside a quartz cylinder in order to allow experiments under controlled atmospheres. The incoming concentrated radiation is deflected by 90° with a cooled silver mirror. For the temperature measurement, the sample and the reflectance reference must be observed through the cylinder and the mirror.

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Vaporization and Gibbs energy of formation of the Rudlesden-Popper phases in the systems MO-Cr_2O_3-La_2O_3, M = Ca, Sr

D.H. Peck, M. Miller[a] and K.Hilpert

Forschungszentrum Jülich GmbH, 52425 Jülich, Germany,

a) on leave from: Wroclaw University of Technology, Wyb. St. Wyspianskiego 27, 50-370 Wroclaw, Poland

Perovskites on the basis of $LaCrO_3$ doped with the second group elements Ca and Sr are of interest as interconnect material in Solid Oxide Fuel Cell (SOFC) technology. Knowledge on the thermochemical stability of these phases under oxidizing and reduced atmosphere is, therefore, of interest for the understanding of degradation processes under operating conditions such as chemical reactions at the interfaces and vaporization.

Samples of the MO-Cr_2O_3-La_2O_3 systems, M = Ca, Sr, of different chemical and phase compositions were prepared by decomposition of the nitrates of the component cations and characterized by means of XRD and electron probe microanalysis. The samples were annealed at 1873 K under low oxygen pressure ($p(O_2) \cong 10^{-9}$ bar) and quenched subsequently. The different ternary Ruddlesen-Popper phases with the general chemical formula $La_nMCr_nO_{3n+1}$, M = Ca, Sr, n = 1, 2, 3, were identified in the samples in addition to the ternary perovskite and binary phases stable under low oxygen pressure (1, 2).

The equilibrium vapor composition over the three phase samples containing the Ruddlesden-Popper phases $LaMCrO_4$, $La_2MCr_2O_7$, and $La_3MCr_3O_{10}$, M = Ca, Sr, was investigated by the Knudsen effusion mass spectrometry at the temperature of 2000 K. The gaseuos species Cr, CrO, CrO_2, M, SrO, and LaO were identified and their partial pressures evaluated. Thermodynamic activities of the component oxides in the samples were calculated by the comparison with the vapor composition of the respective pure oxides. The Gibbs free energy of formation of the Ruddlesden-Popper phases was computed from the activities obtained for different samples containing the same Ruddlesden-Popper phase as one of the condensed equilibrium phases.

1. D.H. Peck, M. Miller, and K. Hilpert, Solid State Ionics, in press.
2. D.H. Peck, M. Miller, and K. Hilpert, Solid State Ionics, in press.

THERMODYNAMIC STUDY OF GASEOUS TERNARY ALKALINE EARTH METAL-BORON-OXYGEN MOLECULES

S.I.Lopatin, G.A.Semenov, D.O.Kirsanov, S.M.Shugurov

St. Petersburg State University, Chemical Department, Universitetskii pr. 2, p/o Stary Peterhof, 198904, St. Petersburg RUSSIA

Available thermodynamic data on vapor species in the alkaline earth metal oxides and boron oxide systems are quite uncertain despite growing interest in the behaviour of these substances at high temperatures. Chemical forms of alkali-containing vapors have been found to be mainly alkali metaborates and their dimers. However, the chemical forms of alkaline earth-containing vapors are still disputable.

A mass spectrometric Knudsen effusion method has been used for the study of the vaporization of $MO{\cdot}B_2O_3$ and $2MO{\cdot}B_2O_3$ (M=Ca, Sr, Ba) in the temperature range 1500-2000 K. The samples were prepared by heating mixtures of M_2CO_3 and B_2O_3 in platinum crucibles at 1300 K for 2 h and were vaporized from platinum and molybdenum effusion cells. In the mass spectra of vapor measured at 25 eV electron energy, the ions M^+, MO^+, BO^+, BO_2^+, $B_2O_3^+$ and MBO_2^+ have been registered. In order to determine the composition of vapor phase, the ions were identified by their appearance energies. Vapor species of M, MO, BO, B_2O_3, MBO_2 and MB_2O_4 have been found. From their partial pressures the standard enthalpies of formation and atomization were determined.

The results obtained in the present work are very useful for understanding the thermochemical properties of inorganic oxyacid salts.

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MASS SPECTROMETRIC STUDY OF THE VAPORIZATION OF CESIUM TUNGSTATE

S.I.Lopatin, G.A.Semenov, T.S.Pilyugina

St. Petersburg State University, Chemical Department, Universitetskii pr. 2, p/o
Stary Peterhof, 198904, St. Petersburg RUSSIA

The process of vaporization of cesium tungstate was studied by the Knudsen effusion method with a mass spectrometric analysis of the vapor composition. The samples were vaporized from the platinum effusion cell heated by resistance furnace. The temperature was measured with a Pt-Pt/Rh thermocouple. The appearance energies (AE) of the ions have been measured by the vanishing current method with Ag (evaporated from Mo cell) as a potential standard, usually accuracy was ±0.3 eV.

In mass spectra of vapor over measured at 25 electron energy, in the temperature range 1000-1100 K, the ions Cs^+ and in a relation 100 : 4.5 have been registered. AE of these ions were 8.5 and 6.5 eV respectively. It has been demonstrated that only $Cs_2WO_4^+$ is parent.

For vapor pressure measurements we used the isothermal evaporation method. The temperature dependence of the Cs^+ and $Cs_2WO_4^+$ –ion currents was measured in the mass spectrum over solid Cs_2WO_4, and the enthalpy of sublimation by the second-law method was calculated between 1017 and 1209 K. In order to lead the sublimation enthalpy to standard condition for Cs_2WO_4(gas) the thermodynamic functions have been calculated by the statistical-thermodynamic method. The $\Delta_sH^\circ(298) = 360\pm7$ kJ, the standard enthalpies of formation and atomization of Cs_2WO_4(gas) are -1594.1 ± 4.2 and 3230 ± 8 kJ/mol respectively.

Enhanced Evaporation of Copper by NH_3 Gas Blowing

Katsutoshi ONO and Ryosuke O. SUZUKI

Department of Energy Science and Technology,
Kyoto University,
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501 Japan

Evaporation from liquid pure copper by top-blowing of NH_3 gas was found. It was visualized by the laser-light sheet method that a large amount of copper smoke takes off from the molten surface attacked by NH_3 gas. The condensates of the smoke were fine spherical copper particles. Evaporation at atmospheric pressure was enhanced by mixing a small amount of N_2 or H_2 gas with NH_3 gas. The formation of an unstable and volatile copper compound was suggested in addition to the cooling effect due to endothermal decomposition of NH_3 gas.

Based on these finding that blowing of NH_3 gas onto molten copper causes its evaporation of enormously high rate, the attempts of NH_3 gas blowing under reduced pressure was applied to the elimination of copper dissolved in molten steel. Typical behaviors of molten steel by NH_3 gas are boiling, splashing and in a violent case slopping from the crucible. The decuprization rate from the molten steel was measured by using a vacuum induction furnace and blowing NH_3 gas through a vertical water-cooled copper nozzle. The rate constant for copper elimination from a flat and smooth surface of molten steel was the order of $2x10^{-3}m\ min^{-1}$ at 1900 K and the pressure range of 10^2 to 10^4Pa.

Because the boiling phenomena are accompanied by an immense increase in the surface area from which volatile species are able to evaporate, NH_3 gas blowing is useful to reduce the decuprization time. Nitrogen concentration in the molten steel increases with increasing the flow rate of NH_3 gas. This supersaturated nitrogen was reduced down to the initial level by vacuum degassing after stopping NH_3 gas blowing.

A34

HIGH TEMPERATURE MASS SPECTROMETRIC INVESTIGATION OF REFRACTORY MIXED OXIDES

László Bencze* and **Arkadij Popovič**

Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

The high temperature evaporation behaviour of Ba_2CaWO_6, $Ba_{0.25}Sr_{0.75}Y_{2.08}O_4$ and $Ba_{0.50}Sr_{0.50}Y_{2.08}O_4$ has been studied between 1273 and 1773 K temperature range in tungsten Knudsen cell by Knudsen effusion mass spectrometry (KEMS), and the results were compared. During the incongruent evaporation of $Ba_2CaWO_6(s)$ in tungsten cell Ba(g), Ca(g), BaO(g) and $BaWO_4(g)$ species are formed whereas during the evaporation of $Ba_{0.25}Sr_{0.75}Y_{2.08}O_4(s)$ and $Ba_{0.50}Sr_{0.50}Y_{2.08}O_4(s)$ only Ba(g), Sr(g) and BaO(g) could be observed. A possible reaction mechanism for the complex evaporation of $Ba_2CaWO_6(s)$ has been proposed by Bhalla, Hirayama *et al.* and Popovic *et al.* previously [1,2,3]. The assignment of the positive ions formed in the equilibrium vapour over the samples was determined by means of the ionization efficiency curves (IEC) and the Clausius-Clapeyron plots. The vapour composition, the equilibrium partial pressures and the thermodynamic properties have been determined for the applied temperature range.

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*On leave from Eötvös Loránd University, Dept. of Physical Chemistry, 1117 Budapest, Pázmány Péter sétány 1/A, Hungary.

Ionisation of gaseous CoF_3 by electron impact. Mass Spectrometric and quantum chemical studies

A. Popovich, A. Lesar, J.V. Rau[1] and L. Bencze[2]

Josef Stefan Institute, Jamova 39, Ljubljana, Slovenia

[1]Chemistry Department, Moscow State University, 119899 Moscow, Russia
[2]On leave from Eötvös Lorand University, Budapest, Hungary

Ionisation and appearance energies of ions formed by electron impact of CoF_3 molecule has been determined using Vogt deconvolution method and the results compared with theoretical calculations. A nonlocal density functional methods (B3LYP) predicts the vertical ionisation energy of 13.1eV. The calculations were performed using the relativistic effective core potential of Stevens *et al.* and the all-electron 6-316(d) basic set for the cobalt and the fluorine atoms, respectively.

The relative partial ionisation cross section curves were also measured in the range from threshold to 100eV using magnetic mass spectrometer, equipped with well tuned ion source of Nier type. In addition, the saturated vapour pressure was measured using Knudsen effusion mass loss method combined with mass spectrometry. A special attention was paid to the change of the sample composition during evaporation. The results were used for critical assessment of the second and the third law sublimation enthalpies.

A36

Bond Energies from Mass Spectrometric Equilibrium Measurements at Very High Temperatures

K. A. Gingerich
Texas A&M University, Department of Chemistry
P. O. Box 30012
College Station, TX 77842-3012 USA

The Knudsen cell method combined with mass spectrometric analysis of the effusing vapor is the most universal tool for measuring homogeneous and heterogeneous equilibria involving diatomic molecules and small clusters at very high temperatures.

We have applied this method at temperatures of 2300 –3000 K to determine the atomization energies and enthalpies of formation of diatomic transition metals, of small carbon clusters and of binary and ternary metallo-carbon clusters, such as MC_n, M_2C_n ($n = 1$-8) and $M_aM_bC_n$ ($n = 1$-4), where M is a transition metal.

A summary of our results will be presented and discussed as they relate to investigations under non-equilibrium conditions of similar, larger clusters, such as fullerenes, metallo fullerenes and metcars.

This work has been supported by the Robert A. Welch Foundation and the National Science Foundation.

Spectroscopic Evidence for the Magnetic Behaviour of Rhodium and Ruthenium Clusters

J. Morenzin, H. Kietzmann, G. Ganteför, P. S. Bechthold, and W. Eberhardt

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

The electronic properties and magnetism of Rh_n and Ru_n clusters (n=1-21) are studied using photodetachment spectroscopy of cluster anions. With increasing n the molecule-like spectral structures observed for the smaller clusters rapidly develop into broader bands. The electron affinity of small rhodium clusters shows an even odd alternation while the electron affinity of ruthenium clusters does not. This indicates a more s,p derived electronic ground state and a relatively stronger localization of d-orbitals in rhodium clusters than for ruthenium. These observations are in accordance with the previously observed larger magnetic moments of the rhodium clusters.

A38

«SYNTHESIS AND THERMODYNAMIC PROPERTIES OF HIGHER BUCKMINSTERFULLERENE FLUORIDES $C_{60}F_{2n}$ (n = 17-24)».

A.S. Alikhanyan, M.I. Nikitin, D.V. Sevast'yanov, A.L. Emelina, V.F. Sukhoverkhov.
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninskii prospect, 117907 GSP-1, Moscow, Russia

In the past few years considerable progress has been made towards synthesis of fullerene C_{60} fluorides including higher ones [1,2]. However, attempts to obtain their thermodynamic characteristics have not yet met with success due to a set of experimental difficulties.

This work is devoted to the synthesis and investigation of thermodynamic properties of higher fullerene C_{60} fluorides. To this end systems based on buckminsterfullerene and d-, f-metal fluorides (CoF_3, MnF_3, K_2NiF_6, TbF_4) have been studied using the effusion Knudsen method with mass spectral analysis of the sublimation products. The gas phase over these systems was demonstrated to contain higher fluorinated fullerenes:

$$C_{60}(s., g.) + 2nMF_m(s., g.) = C_{60}F_{2n}(g.) + 2nMF_{m-1}(s., g.),$$

where n = 17-24. We failed to determine thermodynamic properties of $C_{60}F_{2n}(g.)$ by studying heterogeneous equilibria of this sort. It turned out that in Knudsen cell the equilibrium between the components of the above-mentioned reaction was not established. We believe that in this instance the rate of fluorination of C_{60} is much less than that of the effusion of gaseous components and that of the decomposition of fluorinating agent (d-, f- metal fluoride). To attain an equilibrium, a substance («fluorine trap») which reacts with fluorine yielding a compound with high thermal stability, was introduced into a nickel effusion cell. Molybdenum trifluoride, uranium tetrafluoride and tungsten were used as «fluorine traps». This experimental procedure allowed us to determine the standard enthalpies of formation and the average enthalpies of a C-F bond for $C_{60}F_{2n}$(g.). The general principles of selective synthesis of fullerene C_{60} fluorides were stated.

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A39

Vaporization in system $C_{60}F_{2n}O_m$ (n=21-23; m=0,1)

Emelina A.L., Alikhanyan A.S.,.Nikitin M.I., Sukhoverkhov V.F.

Kurnakov Institute of General and Inorganic Chemistry, RAS, Moscow, 117907, Russia

The fullerenes are able to form a great deal of fluorine adducts. However only four of them ($C_{60}F_{18}$, $C_{60}F_{36}$, $C_{60}F_{46}$ и $C_{60}F_{48}$) have been synthesized in individual state and studied while synthesis other compounds differing in C/F causes to formation of $C_{60}F_{2n}$ mixtures. As far as it is very difficult to separate the mixtures, the thermodynamic properties of compounds in question are still uncertain.

In present work the systems of oxofluorinated fullerenes $C_{60}F_{2n}O_m$ (n=21-23; m=0,1) were studied by an effusion Knudsen method with mass-spectral analysis of the gas-phase composition. The data on isothermal evaporation of sample differing in composition indicated that the solid mixtures containing $C_{60}F_{2n}$ with short range of n appear to be perfect solutions. Using this conjecture one can count reference pressures of mixture components in terms of Raul's low. When the pressures determined the mistakes to make due to presence in perfluorinated fullerenes mass-spectra of low-molecular ions $C_xF_y^+$ signals (to illustrate - CF_3^+) must be taken into consideration, so we made attempt to study nature of the ions. The information on gas-phase composition of studied fluorinated fullerenes mixtures at different temperatures proved the presence of thermodynamic eqilibria among their components. It should be stressed that under this assumption it became possible to make semi-empirical calculations of some important thermodynamics functions. Using these data we also determined the sublimation enthalpies of $C_{60}F_{42}$, $C_{60}F_{44}$, $C_{60}F_{44}O$ and $C_{60}F_{46}$ and obtained the compounds pressure-temperature dependence curves.

A40

The interaction of [60]fullerene with molecular fluorine in the $C_{60}(s)$ -$MnF_2(s)$, $C_{60}(s)$-$Mn_2F_5(s)$ and $C_{60}(s)$ - $MnF_3(s)$ systems

N. S. Chilingarov, A.V. Nikitin, J. V. Rau, I.V. Golyshevskij, A.V. Kepman,
and L.N. Sidorov
Chemistry department, Moscow State University, 119899 Moscow, Russia,
e-mail: nsc@phys.chem.msu.ru

$C_{60}F_{2n}$ (n = 1 ÷ 24) fluorides were detected as the products of $C_{60}(s)$ fluorination by molecular fluorine at T = 500 - 800 K and $P(F_2) = 10^{-5} - 10^{-4}$ atm. The variation of the temperature and the fluorine pressure did not result in the formation of a selective product of fluorination. Along with this, the presence of NiF_2 in an initial weighted portion led to a predominance of $C_{60}F_{18}$ concentration in the gaseous product mixture. The purpose of this work was to study the C_{60} fluorination by molecular fluorine in the presence of manganese fluorides.

The original experimental setup was used, where the synthesis *in situ* and the determination of the gaseous fluorination products composition were carried out. Samples were prepared by careful mixing and trituration of fine crystalline powders of C_{60} (99,9% HPLC) and MnF_2. Weighed portions of given composition were loaded into a reactor. As soon as fluorination temperature was reached the molecular fluorine (98%) entered the reactor through an orifice (d = 0.2 mm) from an external reservoir. Gas phase species escaped through the effusion orifice (d = 0.3 mm) and were analyzed mass spectrometrically.

During each experimental run the composition of fluorination products was determined at fixed temperature of the reactor and F_2 admission inlet. The selection of the optimal parameters was based on the whole set of experimental data obtained under different temperatures and compositions of initial mixture. To check the establishment of the equilibrium between gaseous fluorination products, the results of the experiments performed at the same temperatures but different composition of the initial mixture and F_2 inlet, were compared.

It was unambiguously ascertained that the presence of mangenese fluorides influences the route of [60]fullerene interaction with molecular fluorine. Moreover, the stages of the selective formation of fluorofullerenes could be separated.

Sublimation fullerene hydrides.

M.V. Korobov , P.A. Dorozhko [a], A.S. Lobach [b], A.A. Popov [a], V.M. Senyavin [a]

a) Department of Chemistry, Moscow State University; b) Institute of Chemical Physics at Chernogolovka, Russian Academy of Science

Knudsen cell mass-spectrometry was used to study the thermal behaviour of the solid fullerene hydrides, $C_{60}H_{36}$ (I) and $C_{60}H_{18}$ (II).

The vapour phase over (I) was studied at temperatures 520-670K. The evaporation was performed from quartz effusion cells. The electron impact mass-spectrum was recorded using MI 1201 static mass spectrometer. The resolution of the instrument was around 700. A number of peaks corresponded to the positive ions $C_{60}H_n^+$ were detected. Mass spectrum vs. time dependencies were obtained in isothermal runs at T=594 and 610K.

It was shown that the isothermal treatment of (I) led first to the formation of (II) and than to the de-hydrogenation of the sample, the composition of the remaining solid phase being approximately "$C_{60}H_6$". The decomposition was accompanied by the sublimation of $C_{60}H_{36}$ and $C_{60}H_{18}$ vapour species. Ion currents, corresponded to the mass numbers m/e = 762 and 764 (possibly, vapour species $C_{60}H_{42}$ and $C_{60}H_{44}$) also appeared in the mass spectrum while heating of the sample after 20 hrs. The remaining solid was hardly soluble in organic solvents.

The de-hydrogenation/sublimation process was strongly affected by the material of the effusion cell (Ni, Pt, Au) and the purity of the initial sample. The saturated vapour pressures of $C_{60}H_{36}$ and $C_{60}H_{18}$ were estimated to be $9,8 \cdot 10^{-8}$ atm and $5,4 \cdot 10^{-8}$ atm respectively at T=594 K. At the same temperature under vacuum 48% of the initial amount of hydrogen in the solid phase was removed as H_2(gas) while the rest was incorporated into the $C_{60}H_n$ species.

The second law sublimation enthalpies of $C_{60}H_{36}$ and $C_{60}H_{18}$ at 520-650K were determined as 164±8 kJ/mol and 166±5 kJ/mol, respectively. These numbers were compared with the third law results.

This study was supported by the Russian State Program "Fullerenes and Atomic Clusters"

A42

SPECTROSCOPIC INVESTIGATIONS ON HIGH TEMPERATURE MOLECULES

K. P. R. Nair* and F. W. Froben**
*Department of Physics
Cochin University of Science and Technology
Cochin-682022, India

and

**Institut für Experimentalphysik
Freie Univerität Berlin
Arnimallee-14
D-14195 Berlin

Recent spectroscopic investigations on a number of diatomic molecules have shown systematic variations in many molecular parameters like nuclear hyperfine constants, electric dipole moments etc. These molecules were produced at high temperatures. The microwave investigations on a number of diatomic molecules will be presented. The production of these molecules at hight temperatures, analysis and systematic variations in molecular constants give interesting information on molecular structure and interactions.

Dimerisation Of The Rare-Earth Halides

C. P. Groen, A. Oskam and E. H. P. Cordfunke

Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018WV, Amsterdam, The Netherlands.

Since the identification of a dimer homocomplex in the equilibrium vapour above solid $LaCl_3$ [1], numerous studies, mostly mass spectroscopic, on other rare-earth halides were focused on an accurate description of the vapour composition. The thermophysical and thermodynamic functions of the gaseous species involved, necessary for a correct interpretation of results, were only available as estimations. This has led to controversy in literature data concerning the composition of equilibrium vapours of several rare-earth halides.

Our study intends to reduce the ambiguity among published equilibrium vapour compositions. We therefore derived new thermodynamic functions from our matrix-isolation and gas-phase vibrational spectroscopic experiments in conjunction with gas-phase electron diffraction experiments and *ab initio* calculations.

The functions are used to evaluate the existing experimental data from literature. Thermodynamic data of the dimerisation process have been derived, and trends with physical parameters, such as atomic number and radius, are presented. The accuracy of the results will be discussed.

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A44

The Influence of different Types of Quartzglass used as Lamp Tubing on the Performance of Modern Light Sources

Ralf Takke, Heraeus Quarzglas GmbH & Co KG, Quarzstraße, D-63450 Hanau, Germany

Hans-Dieter Witzke, Heraeus Noblelight GmbH, Heraeusstraße 12 – 14, D-63450 Hanau, Germany

The trend in modern light source development clearly points towards miniaturization with the effect of higher radiation fluence for the lamp envelope. Simultaneously lifetime is of importance for obvious reasons. This means that the physical and chemical properties and the performance of the lamp envelope-material contributes more and more to the success of a lamp in the marketplace.

In this paper we describe the properties of different types of quartzglass, the most common lamp envelope material, in terms of transmission in the UV, outgassing, viscosity, mechanical stability, solarization resistance and fluorescence.These properties will be discussed in terms of quartz raw material properties, the production process of quartzglass and the thermal history of the lamp tubing.

A Cerium doped quartzglass lamp tubing is used as an example to show how the microchemistry within the lamp wall is influenced by thermal processing and itself is influencing the physical properties like transmission and fluorescence during lamp operation. Additionally for high power DUV – excimer lamps the influence of different types of synthetic quartzglass on the lamp performance will be discussed.

It will be shown how a deeper understanding of the lamp wall chemistry is helpful in producing quartzglass taylored to the requirements of the lamp manufacturer.

A45

Metal-Ceramic and Ceramic-Ceramic Interfaces and Their Applications

By

Alfred E. Feuersanger
Rease Group, 66 Overlook Drive, Framingham, MA, USA*

Materials research on the high temperature behavior of semiconductors and metals is advanced and relatively mature. For semiconductors growth of very large defect free single crystals and multi-step device processing, often in conjunction with thin films, are state of the art problems. However, multiphase ceramics and alloys, on the other hand, are usually polycrystalline and are not understood theoretically in great detail, although their fabrication is reproducible by mostly empirical processes. The ceramic- ceramic and the ceramic-metal interfaces are found in many important components in scientific and technological applications, e.g. vacuum feedthroughs, optical windows and high temperature and high pressure vessels.

In both during formation (usually [illegible] ceramic high temperature firing process) and during operation in applications, the adjacent solids and interfaces have to maintain mechanical strength, structural integrity, electrical and dielectric loss performance, chemical reaction compatibility, and thermal behavior. Due to the difference in chemical composition of the solids, their interface is a discontinuity in many of these properties. For the ceramic-ceramic case with multi-phases, segregation of phases and grain growth with anisotropic properties can occur and have been observed. For the metal-ceramic case minor impurities in the gas atmosphere during firing can cause chemical reactions that become the primary factor in controlling the process. Criteria have been established for minimizing these effects in a number of practical processes. Modern surface analytical techniques have been invaluable in characterizing the interfaces and in process development.

In these heterogeneous systems a stress field is generated at the interface due to the difference in temperature coefficients of expansion that cover the range of temperatures. To compensate for the mismatch, interlayers are applied to the ceramic and the metal is then brazed on for medium temperature (~350 C) operation. For high temperatures (~1200 C), complete matching over the whole temperature range is required. This and requirements for chemical stability limit the available material choices severely in many applications.

The ceramic and metal-ceramic interfaces play an important part in advanced devices. They must operate under the most severe material conditions and must have a long life.

For some examples, the design of ceramic-ceramic closures and of ceramic-metal electrically conducting feedthroughs for optically transparent vessels, operating at high temperature and pressure, are discussed.

Abstract for 10th Int. IUPAC Conference on High Temperature Materials Chemistry.
10-14 April 2000, Juelich, Germany.

* GTE Laboratories Inc. Waltham, MA, 02254 USA, retired.

A46

A SIMPLE Δλ-METHOD FOR ROUTINE MEASUREMENTS OF ATOMIC PARTIAL PRESSURES IN BURNING HID LAMPS

Achim Körber

Philips Research Laboratories, Weisshausstr. 2, D 52066 Aachen, Germany

1 INTRODUCTION

For a detailed knowledge of the chemistry within the gas phase of a high intensity discharge (HID) lamp it is essential to determine the *partial pressures* p_x of impurities or the dosed elements preferably in a non-destructive way during lamp life.

2 PRINCIPLE

Measured quantity is the wavelength distance Δλ between the self-reversal maxima of an optically thick line of the element in question. If the line is not too strong (i.e. $\Delta\lambda < 5$ Å) and the pressure broadening is dominated by van der Waals interaction of species x with the buffer gas (e.g. rare gas or Hg), the "impact approximation" is valid which means that the line shape will be Lorentzian and the relation between Δλ and the atomic partial pressure p_x , the buffer gas pressure p_{Buf} and the inner vessel radius R_i will be of the simple form

$$\Delta\lambda = \text{const.} \cdot \sqrt{p_x \cdot p_{Buf} \cdot R_i} \quad \text{or} \quad p_x = \frac{\Delta\lambda^2}{\text{const.}^2 \cdot p_{Buf} \cdot R_i} \tag{1}$$

involving only *one* proportionality constant to be determined for each specific case.

3 SET-UP

A highly-resolving spectrograph (focal length ≈ 1 m) is necessary to obtain Δλ with sufficient resolution. Best results will be obtained with a side-on projection, but for comparisons of lamps with identical geometry an "integrating sphere" measurement proved to be sufficient.

4 ACCURACY & PRESSURE RANGE

The method is best suited for *resonance lines* where the influence of the plasma temperature profile on the occupation of the absorbing state is negligible. Then the statistical error $\text{rel}\sigma_{px}$ will be typically in the order of 12 %. Pressures between ≈ 10^{-5} bar and 10^{2} bar may be measured - depending on the broadening constant and lower level of the chosen line. However, the spectral resolution of the monochromator (≈ 0.2 Å) and the constraint $\Delta\lambda < 5$ Å limit the dynamic range for *one specific line* to about two orders of magnitude.

5 VERIFICATION

The method has been tested to work properly for determining the partial pressures of Sn, Hg, Hf, Ti, Al, Ca and Y in lamps with several bars of mercury as buffergas.

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THE HF-ELECTRODELESS LIGHT SOURCE CLEANING METHOD

A. Skudra, N. Denisova*, G. Revalde.
Institute of Atomic Physics and Spectroscopy, University of Latvia,
Raina blvd. 19, LV 1586, Riga, Latvia
*Institute of Theoretical and Applied Mechanics, 630090, Novosibirsk, Russia

High-frequency electrodeless light sources are known as intensive spectral line emitters in bright spectral region: from infrared to VUV. Because of lack of electrodes it seems like these light sources are living forever but there is another process restricting source lifetime: interaction of filling element with walls of the glass bulb. This process depends strongly from the light source operating power. To prevent this process the rare gas as a buffer gas could be added. In [1] gases coming out of walls of source vessel has been measured by means of mass-spectrometry. There the training method using discharge in the rare gas was suggested to clean the light source walls from pollution.

For the diagnostics of interaction between filling element and source walls we have prepared hf electrodeless light source samples filled only with helium of various pressure. The emission spectrum of inductively coupled discharge was registered. There were observed not only helium spectral lines, but also oxygen, hydrogen and carbon spectral lines coming out from the walls. Several techniques can be used to clean source vessels. Commonly, the training of the source vessel is performed with the same rare gas which is provided for filling. We have tried to use also other rare gases for this goal. We have compared spectral line emission from elements mentioned above for different training techniques. In Fig.1 are shown the 728,1 nm helium spectral line intensities, emitted from pure He light source in dependence from discharge current for three cases: 1) source without training, 2) source vessel trained in helium discharge, 3) source vessel trained in krypton discharge.

We can see that the light source vessel training with krypton is more effective: He spectral lines have higher intensity as by common training method. The intensity dependence from discharge current without training shows only a little change. In this case the concentration of admixtures coming out from the walls of source is to high and therefore helium line intensities show even a slow decrease. For the commercial application of light sources most important is H-discharge [2]. In our case that is the discharge current region higher as 160 mA. This is just the region in which the amount of oxygen coming out from walls has maximum. This emission of oxygen could serve as characteristic value for interaction of the filling element with walls. That means that in this region just the interaction is higher.

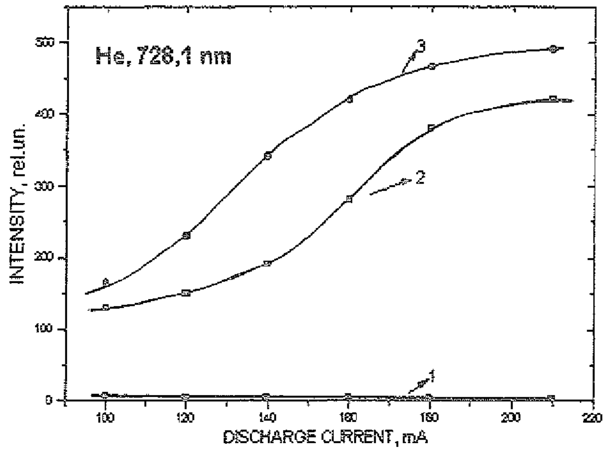

Fig. 1. He 728,1 nm spectral line intensity from He source in dependence of discharge current for 1-source without training, 2- from source trained in He discharge, 3- from source trained in Kr discharge.

Our experiment shows that the oxygen lines are most intensive in the region of He pressure from 0.5 till 1.5 Torr. This is also the optimum region for He line emission.

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A48

OPTIMUM OF FILLING OF RARE GAS AND HYDROGEN HF-ELECTRODELESS LIGHT SOURCES

G. Revalde, A. Skudra.
Institute of Atomic Physics and Spectroscopy, University of Latvia,
Raina blvd. 19, LV 1586, Riga, Latvia

High-frequency electrodeless light sources (HFELS) are filled with a working element (mostly, metal) and buffer gas (mostly, rare gas). The rare gas in the high-frequency (HF) discharge have two functions: on the first, they have to serve for the ignition of discharge in a cold light source. The discharge in the rare gas causes an increase of the temperature of the source. Only when the temperature is high enough to evaporate some part of the working element, the main discharge can be started. On the other side, the rare gas delays the interaction of the working element species with the material of source walls. This allows to increase the life time of the light source. For the understanding of processes, taking place in such radiators, it is more appropriate to investigate discharge in a pure rare gas [1,2].

We investigate the high-frequency electrodeless discharge in helium, neon, argon, krypton, xenon and hydrogen in order to find optimal pressure for HF - discharge. The intensities of emission spectral lines from light source samples on-line with vacuum-system was measured as a functions of the gas pressure. The inductive coupled discharge was effected by placing the light source in the coil of high-frequency oscillator working on approximately 100 MHz frequency. By means of optical fibre emitted light was transmitted through a monochromator, and the relative spectral line intensity was registered by a photomultiplier.

We have seen, that the dependencies of intensity versus the pressure for spectral lines of xenon, krypton and argon was of the same kind. From the maximum intensity of several spectral lines we determined the optimum of the filling element pressure. The maxima of the spectral line intensities of the most lighter gases-helium and neon-lie at much higher pressure than for the heavier gases.

The especial interest was devoted to the hydrogen HFELS technology because of wide use of these lamps in atmospheric investigations. There is a problem of easy penetrating of hydrogen atoms through the lamp walls. Several methods must be developed in order to increase the life time and intensity of the hydrogen HFELS [3]. In fig.1 are plotted the measured intensities of spectral lines λ_1 = 656.3 nm and λ_2 = 486.1 nm, emitted from hydrogen HF-discharge, as a functions of the hydrogen pressure. The maxims of these dependencies are located at lower pressure values than for lighter rare gases: helium and neon. It could be explained by the necessity of dissociation of hydrogen molecules H_2 before the excitation of hydrogen atom H.

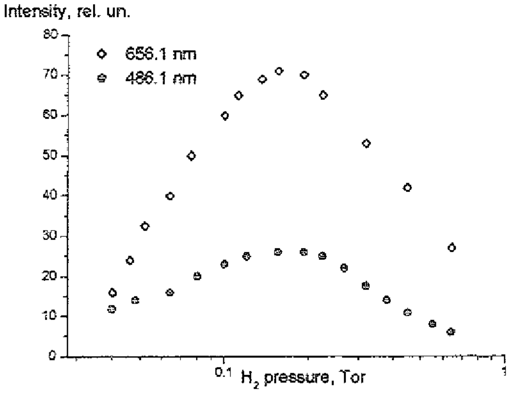

Fig. 1. The intensity changes of hydrogen atomic spectral lines versus the hydrogen pressure

We have shown that the values of the gas pressure being optimal for high-frequency electrodeless discharge for light rare gases, such as neon and helium, are about of two orders higher than for heavier rare gases: xenon and krypton. The value of optimum pressure for hydrogen is laying approximately in the same range than for heavier rare gases. From our observations we can conclude that the optimum pressure for well conditioned HF-discharge in rare gases and hydrogen roughly is not dependent on the excitation power.

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A 49

INTERACTION OF ZINC WITH RARE-EARTH HALIDES UNDER CONDITIONS OF HIGH-PRESSURE DISCHARGE LAMPS

Matthias Born and Ulrich Niemann
Philips Research Laboratories, Weisshausstr. 2, D 52066 Aachen, Germany

1 INTRODUCTION

Investigations aiming at the replacement of mercury as a buffer gas in high-pressure discharge lamps have revealed that zinc would be a potential candidate for this purpose. As a pre-requisite, however, a detailed knowledge of its chemical reactions with common metal halide lamp fillings such as rare-earth halides is required.

2 EXPERIMENTAL SET-UP

Chemical transport experiments have been performed in quartz ampoules in the range of typical coldest spot temperatures (700 to 1000°C) applying various NaI/LnI_3 (Ln = rare-earth metal) molten salt mixtures in molar ratios varying between 2:1 and 10:1.

3 EXPERIMENTAL RESULTS

Since no interaction between NaI and zinc could be found, the amount of ZnI_2 formed during reaction was used as a relative measure for the overall reaction with LnI_3. The degree of reaction was similar for different rare-earth metals applied; it increased, however, significantly with higher temperatures and decreasing molar ratios of the molten salts applied. Chemical analysis of the dark, non-volatile residue revealed the presence of LnI_x compounds admixed with large quantities of rare-earth metals.

4 THERMOCHEMICAL MODELLING

The experiments were accompanied by extensive thermochemical modelling. It proved to be impossible to verify all experimental results applying established thermochemical data and solution models. We suspect therefore that under these conditions additionally reactions with the quartz wall have to be taken into account leading to the formation of dark LnOI phases stable between 800 and about 1500°C.

5 CONCLUSIONS

The reduction potential of zinc towards metal halides mixtures NaI/LnI_3 typically applied in high-pressure discharge lamps is considerably higher as compared with mercury. Furthermore a specific influence of wall materials can be stated: The formation of strongly discoloured LnI_x or LnOI phases is less pronounced if reactions are performed in polycrystalline Al_2O_3 (PCA) possibly due to the formation of stable colourless or white rare-earth aluminates stable up to highest temperatures. Therefore the application of zinc together with NaI/LnI_3 mixtures in ceramic discharge tubes proved to be successful.

INVESTIGATION OF PLASMA CORE TEMPERATURE AND ELECTRODE TIP TEMPERATURE IN METAL HALIDE LAMPS CONSIDERING DIFFERENT OPERATING CONDITIONS

D.C. FROMM, G.H. LIEDER, K.H. GLEIXNER

OSRAM GmbH, Hellabrunner Str.1, D-81536 Munich

Main goals in lighting research are directed towards an improvement of *emission properties* (e.g. luminous efficacy, CRI, color appearance), *lumen maintenance* (e.g. by reducing wall blackening) and *lamp life* (e.g. by reducing electrode corrosion). These objectives were achieved hitherto only in an empirical manner. However, recent advances in experimental plasma diagnostics and modeling promise to improve the basic understanding of the manifold of physical and chemical processes in such lamps. Therefore, a new quality of metal halide (MH) lamps is expected in the near future.

A better understanding of the electrode behavior is one of the essential goals to improve the performance of MH lamps. The decrease in lumen maintenance due to electrode corrosion and the following blackening of the inner wall is mainly caused by high electrode temperatures and additionally in the case of conventional ballast operation by reignition spikes.

The plasma temperature which determines the radiation characteristics and the dynamics of transport processes and chemical reactions is one of the most important parameters in MH lamps. In this context influences of axial segregation on the plasma temperature in front of the electrodes and possible interactions with the electrode tip temperature has to be taken into account by special investigations.

An universal spectroscopic instrument which allows spatial, temporal and phase-resolved measurements on commercial HID lamps has been set up in order to investigate profiles of electrode temperature and plasma temperature. The absolute accuracy of the pyrometric measurements of the electrode temperature was ± 30 K, while the determination of the plasma core temperature, using a modified Bartels method, has an accuracy of ± 100 K. During the measurements different parameters have been varied as waveform and frequency of the ballasts employed, either electronic or conventional, also the filling (one or multi-component system) and the operating position (horizontal or vertical).

There is a close correlation between the electrode tip temperature (T_t) and the plasma temperature in front of the electrode (T_p) due to the influence of the *cataphoresis*. If T_p is reduced at the cathode the T_t-value of the cathode is also decreased simultaneously, whereas T_p in front of the anode is increased together with the corresponding T_t-value. This effect reaches its maximum in the DC case and disappears at operating frequencies above 100 Hz. It is caused by an increase of the ion density at the cathode where ions take a greater part of the total current. Therefore, the cathode has to emit less electrons which corresponds to a lower value of T_t.

From these results it is deducible that optimal conditions in terms of lumen maintenance and lamp life are achieved when the electrode temperature difference between anode and cathode phase is minimized and if reignition spikes are avoided. It will be shown that both requirements can be fulfilled by a rectangular current waveform (switched DC) within a optimum frequency range of about 120 Hz to 200 Hz and a horizontal operating position of the MH lamp. Moreover, the bad influence of axial segregation on the radiation distribution of such lamps is also suppressed.

With these results, a further step has been made towards a better understanding of the complex physical and chemical processes in MH lamps.

Vapour pressure of TlI and its influence on the partial pressure of Tl in metal halide lamps

B. Schalk and L. Hitzschke, OSRAM GmbH, Hellabrunner Straße 1, D-81543 München, Germany
G. Hartel, Ribnitzer Straße 13, D-18181 Graal-Müritz, Germany

For the calculation of electrical properties and emitted radiation of metal halide lamps knowledge of the partial pressure of Tl in the arc plasma is of high importance. Due to its lower ionisation energy in comparison with Hg it works as the main electron supplier, its spectrum gives an important contribution to the radiation of the lamp.

In this poster results on metal halide lamps will be presented. The examined lamps contain Hg and TlI. Because the filled in condensed TlI is not completely vaporised, the amount of Tl in the arc plasma can not directly be determined.

However, if the lowest temperature on the inner lamp surface, the cold-spot temperature, is known, the partial pressure of TlI in the arc plasma is given as the vapour pressure of the TlI melt at this temperature. The cold-spot temperature is taken from thermographic measurements, the vapour pressure curve is calculated from thermodynamic properties of condensed and gaseous TlI.

On the other hand the partial pressure of Tl can be related to the wavelength separation $\Delta\lambda$ between the maxima of self-reversed optically thick Tl-lines. For this, measured and calculated spectral line profiles of Tl at 535.046 nm ($7s^2S_{1/2} \rightarrow 6p^2P^o_{3/2}$) and 377.572 nm ($7s^2S_{1/2} \rightarrow 6p^2P^o_{1/2}$) are compared. The calculated $\Delta\lambda$ show only a weak dependence on both assumed temperature profile and total pressure in the lamp, but a strong dependence on the amount of Tl in the arc.

Further, by comparing the partial pressures of Tl obtained by both methods, conclusions on the accuracy of the underlying vapour pressure curve will be drawn.

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A reaction-diffusion model of cylindrical halogen lamps

Tamás Turányi *and* Tamás Perger
Department of Physical Chemistry, Eötvös University
H-1518 Budapest, P.O.Box 32, Hungary
and
László Balázs
GE Lighting Tungsram
H-1340 Budapest, Váci út 77, Hungary

In halogen lamps, the envelope is filled with Ar, Kr or N_2, with small amount of CH_3Br or HBr added. The tungsten filament contains trace amount of O_2 adsorbed. In a stationary operating lamp, the filament has a typical temperature of 2900K and the temperature of envelope wall is about 800K. When the lamp is switched on for the first time, all CH_3Br is converted to HBr, C_2H_2, CO, H_2 and other species. Tungsten, evaporated from the filament, is converted to tungsten bromides, oxides, and oxobromides.

All present models of halogen lamps use the assumption of local thermodynamic equilibrium (LTE). This approach is incorrect far from the filament at low temperature and has many limitations. A proper description of halogen lamps must be based on chemical kinetic reaction-diffusion models.

A detailed reaction mechanism of 395 reactions was created that described the oxidative pyrolysis of CH_3Br and the reactions of tungsten compounds. The hydrocarbon reactions were a subset of the Leeds Methane Oxidation Mechanism. The bromine reactions were taken from the NIST CF_3Br combustion mechanism. Rate coefficients of the tungsten compound reactions were calculated on a theoretical basis. An accompanied thermodynamic database was also created that contained the temperature dependence of ΔH, ΔS, and c_p for all 55 species in the form of NASA polynomials. A transport database included diffusion and thermal diffusion coefficients for all species.

A computer code was written for the simulation of halogen lamps as a 1D cylindrical reaction-diffusion system. The balance equation for each species included diffusion, thermal diffusion, thermal and photochemical reactions. A stiff PDE solver calculated the stationary concentration profiles as a function of distance from the center of the envelope. These profiles were in good qualitative and semi-quantitative agreement with experimental data.

Normal Spectral Emittance Measurements (600-2000 nm) of Polycrystalline Alumina (PCA) at High Temperatures

Laurence Bigio*
GE Corporate Research and Development Center
P.O. Box 8, Building K1-4C21
Schenectady, N.Y. 12309

* After Aug. 30, 1999: GE Lighting, Nela Park, 1975 Noble Rd., Cleveland, OH 44112

A novel method is shown for measuring the spectral emittance of polycrystalline alumina (PCA) in the temperature range ~1100-1400 C, from 600-2000 nm. The method utilizes a CO_2 laser at 10.6 microns to heat a ~4 mm size spot on a small sample (~6x4 mm) from one side, while the temperature and emission are measured optically from the other side. A fiber optic radiance probe focuses on a 2 mm spot in the middle of the larger heated region, and directs the collected emission to a spectrometer system. Radiance measurements are conducted relative to a blackbody at 1000 C. The temperature is measured at the same location viewed by the radiance probe using a thermal imaging pyrometer with a narrow bandpass at 10.6 microns. Since this is the same wavelength as the laser, care must be taken to avoid the scattered laser radiation that partially overfills the sample. An emittance at 10.6 microns of 0.97 is assumed for the temperature measurements. In the spectral region 600-2000 nm, the emittance is found to decrease with increasing wavelength and increase with increasing temperature. A multiple regression fit is presented which enables data interpolation at any wavelength and temperature within the range measured. This method can be used on other ceramic materials as well.

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Dedicated Pinch protection of High Intensity discharge burners

Maarten Steinmann
Philips Lighting B.V., P.O.Box 80020, 5600 JM Eindhoven, The Netherlands

High thermally loaded quartz glass burners suffer from oxidation of the molybdenum feed-through parts during lamp burning, provided no outer bulb is present. Oxidation of the molybdenum parts affects lamp life strongly beyond a critical quartz pinch temperature of 350 oC (IEC norm).

Chromium coating of molybdenum feed-through parts is one of the best protective agents against corrosion and oxidation. If applied, permissible pinch temperatures are far beyond the present critical temperature of 350 oC and increases lamp life substantially. Some lamp applications however only require a higher permissible pinch temperature during burner operation rather then long lamp life. Therefore the level of pinch protection by chromium coating should be well tuned for achieving such specific requirements.

Tuning is done by coating only specific parts of the molybdenum feed-through assembly. Thus, a performance range of pinch protection can be established, corresponding to the extend and distribution of chromium coating that is applied.

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On the role of chemi-ionisation in rare-gas medium pressure discharge lamps

Georges Zissis, Jean-Jacques Damelincourt
CPAT, Univ. P. Sabatier, 118 rte de Narbonne, F-31062 Toulouse cedex 4, France
http://cpat.ups-tlse.fr
Yan-Ming Li, Graeme Lister
OSRAM SYLVANIA INC., 71 Cherry Hill Drive, MA 01984, USA

Electrical discharges in pure rare gases, and more especially in neon and xenon, are often used for specific lighting purposes such as signal lights and more recently for automotive applications (neon discharge) or even for general lighting (xenon discharge). The properties of those discharges were extensively studied during the fist half of 20th century. However, their luminous efficacy is modest and Hg-rare gas mixtures were used widely for light production. Nowadays, as international legislation becomes more severe for mercury-containing products, the interest for pure rare gases is increasing again. An important issue concerns the use of increased rare gas pressure in the discharge (more than 1/3 of atmospheric pressure). Under these conditions, molecular ions such as Ne_2^+ and Xe_2^+ are no longer negligible, but very little is known about the formation channels of these ions in the discharge. In this paper we present a self-consistent collisional-radiative code (SCCR) which allows us to study the formation of such molecular ions in the case of pure neon electrical discharge.

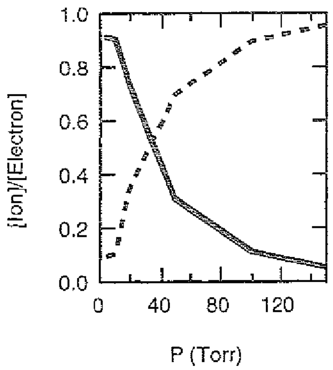

Fig 1. : Solid line Ne^+ doted line Ne_2^+

The Self-Consistent Collisional-Radiative code is based on the excited and charged species balance coupled with the electronic energy conservation equation; the quasi-neutrality condition, perfect gas law and Ohm's law close the equation set. In this model, we consider the Ne atom as a 14 level system (4s and 10p levels), with atomic and molecular ions. Several collisional channels for the formation and destruction of the Ne_2^+ are included: Chemi-ionisation (collision between metastable Ne atoms), ion conversion (from atomic to molecular ion), 3-body association, dissociative ionisation.

The importance of the molecular ion is demonstrated in the Figure 1, since in several cases the molecular ion density becomes higher than the normal atomic ion density. Since charge neutrality is always respected in the positive column, the electron density could be completely controlled by reactions such as atomic ion conversion and balance between associative ionisation and dissociative recombination.

A56

Synthesis, structure and elekctrochemical properties of In-doped $BaTbO_3$

K. Künstler, H.-J. Lang, G. Tomandl
Freiberg University of Mining and Technology, Institute of Ceramic Materials,
D-09596 Freiberg/Germany

Compounds with perovskite structure can be regarded as prospective solid electrolyte or electrode materials for the intermediate temperature range. This structure type features the advantage of variation of elements in the crystal lattice and of simplicity of doping adiovalent cations for the formation of oxygen ion vacancies. The doped $BaCeO_3$ and $BaTbO_3$ were selected from the literature for our investigations. The results for doped $BaCeO_3$ have been explained in several publications. The results for the In-doped $BaTbO_3$ are still pending.

The system $BaTb_{1-x}In_xO_{3-\alpha}$ was prepared in a concentration range $0.05 \leq x \leq 0.25$ mole $InO_{1.5}$ and the physical-chemical properties were determined. The X-ray diffraction analyses of doped $BaTbO_3$-samples featuring relative densities from 92 to 95 % showed perovskite structure. The compound are stable in oxidizing and inert atmospheres. The structure of In-doped $BaTbO_3$ is not influenced by the water vapour partial pressure in the air in the temperature range from 500 to 950 °C. Under reducing conditions the structure of the $BaTbO_3$ is destroyed.

The ICP-OES-analysis was applied for the determination of the elements Ba, Tb and In. The sintered sample always had a higher content of Ce than the mixed powders. BaO and In_2O_3 are a little evaporated during sintering.

Infra-red spectroscopical investigations of In-doped $BaTbO_3$ showed no additions of H_2O and OH groups of the oscillation mode with or without hydrogen bridge linkages. When samples of In-doped $BaTbO_3$ were treated with the gas mixture $CO/CO_2/H_2/H_2O$, OH, CH_2 and the structure elements HCO^-_3 and CO^{2-}_3 were indicated at In-doped $BaTbO_3$.

The electrical total conductivities of various In-doped $BaTbO_3$ were measured by the dc four-point method in air, argon and N_2/H_2 (with 2 vol-% H_2) in the temperature range between 500 and 900 °C. Each of these gases was conducted over the samples, dried with P_2O_5, regular or humidified. The electrical conductivity of In-doped $BaTbO_3$ does not exceed the conductivity of yttria-stabilized zirconia.

The compounds of In-doped $BaTbO_3$ treated under reducing conditions showed already at lower temperatures a good oxygen exchange behaviour. The compound are suitable as electrode material for electrochemical cells.

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Influence of strontium vanadates on the sintering properties of lanthanum manganite

F. Tietz, W. Jungen, P. Lersch
Forschungszentrum Jülich, IWV 1, D-52425 Jülich, Germany

A key problem in realization of a planar solid oxide fuel cell system with ferritic steel as interconnect material [1] is the assembling of the fuel cells at relatively low temperatures around 900°C. For connecting electrically the cathode with the interconnect material, usually ceramic pastes of perovskite powders based on lanthanum cobaltite or manganite are used. The matter for further improvements is the poor adhesion of the ceramic paste to the adjacent components due to the low assembling temperature.

Three compositions in the $SrO-V_2O_3$ phase diagram were synthesized and used as sintering additive to improve the sinterability of $La_{0.65}Sr_{0.3}MnO_3$ (LSM). Because the lowest melting point is 530°C in the Sr-V-O sys[illegible] enhance the densification via liquid phase sintering. Densification curves with various amounts of vanadates were recorded at 900°C using a push-rod dilatometer and conventional sintering experiments in a chamber furnace were performed at 1300°C for 5 h. The specimens were characterized after the sintering experiments by X-ray diffraction (XRD) and ceramography.

The measurements at 900°C revealed lower shrinkage with increasing amount of Sr-rich vanadates. Also Sr-poor vanadates inhibited the densification, but to a smaller extent. Although no change of lattice parameters of the LSM was observed, the XRD patterns showed the formation of $LaVO_4$ and $Sr_3(VO_4)_2$ for samples with more than 3 w/o of sintering additive. Sintering at 1300°C resulted in higher densities of the vanadate-containing specimens than the starting material. A slight increase of lattice parameters of LSM and the formation of Mn_3O_4 and $Sr_2La_{0.67}(VO_4)_2$ were found by XRD.

The results of the sintering experiments show that vanadates interact with but do not increase the sinterability of LSM at low sintering temperatures relevant for SOFC application. However, a beneficial contribution to densification is observed at high sintering temperatures.

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A58

TEMPERATURE DEPENDENCE OF THE FREQUENCY INDEPENDENT FACTOR CPE -EFFECT OF SOLID ELECTROLYTES

O.L.Kobeleva

Ural State University, Physics Dept., Lenina ave.,51, Eketerinburg, 620083, Russia

For many solid electrolytes the dependence admittance from frequency is proportional to a fractional exponent of frequency (CPE effect)

$$Y=B(i\omega)^{\alpha} \qquad (1)$$

In (1) factors B does not depend of frequency. An exponent CPE α depends from temperature and factor B depends from temperature and α. The experimental investigations of dependence B from α [1]-[2] give relation

$$B=C\nu^{1-\alpha} \qquad (2)$$

where ν - constant value (having dimensionality of frequency), C - capacity of ideally smooth contact an electrolyte / electrode.

The purpose of the paper is the theoretical investigation of temperature dependence of a relation (2). For this purpose was used sceiling property of effective capacitance's, resistances and admittance's a double layer [3] - [4] and fractal theory of temperature dependence CPE [5]. It is shown, that B has temperatures dependence coinciding with (2)

$$B=C \qquad \nu^{\alpha_{cp}(T)} \qquad (3)$$

where α_{cp}(Ò), determinated by [5]

$$\alpha_{cp}\ (\mathrm{T})=\frac{\beta\,(1-\exp(-\frac{\alpha_0^2}{2\beta^2}))}{\Phi(\frac{\alpha_0}{\beta(T)})}\sqrt{\frac{2}{\pi}}$$

The relation (3) allows to describe any experimental temperature dependence B(Ò).

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Relationship Between Network Expansion and Average Electronegativity in Superionic Glasses

Masaru ANIYA
Department of Physics, Faculty of Science, Kumamoto University,
Kumamoto 860-8555, Japan

Superionic conducting glasses have attracted considerable interest for the last several years. Investigation of superionic glasses is interesting from both academic and practical points of view. The practical aspect arises from their use as key materials for solid state electrochemical technology. The academic interest arises from the fact that the mechanism of ion transport and related phenomena in superionic glasses remains poorly understood. In particular, the evolution of parameters such as concentration and mobility of free carriers, as a function of composition and temperature, have not been definitively established.

Recently, a remarkable scaling relation between the ionic conductivity enhancement and the network expansion by salt doping in superionic glasses has been found [1]. This finding indicates that the available free volume in the glass is a key parameter determining the increase of the high ionic conductivity.

In the present contribution, the relationship between the average electronegativity of the glass and the network expansion by salt doping is studied. The average electronegativity has been calculated [2] and the network expansion has been obtained from density data. It is found that the network expansion increases as the average electronegativity decreases. Furthermore, it is found that such a relationship can be represented by a single universal curve. This finding is in accordance with the previous result. That is, the existence of the scaling relation between the average electronegativity and the ionic conductivity in superionic glasses [2].

The result of the present work is expected to provide a new way to understand and predict the properties of superionic glasses.

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A 60

Fabrication and Properties of New Composite Powders for SOFC Anodes from a Ceramic Eutectic Melt Process

Ch. Gerk, M. Willert-Porada, University of Bayreuth, Faculty of Applied Natural Sciences, Chair of Materials Processing, 95440 Bayreuth; christian.gerk@uni-bayreuth.de

Ceramic powders containing NiO and 8Y-ZrO_2 in eutectic composition are built up of lamellae of about 0.5 µm width. Such powders are a new and improved type of material for SOFC anodes. The eutectic powder is prepared by melting a mixture of commercial NiO and 8YSZ at 1750°C using either laser or microwave energy. The optimisation of three contradictory properties is made possible by this powder: an extremely high triple phase boundary area, a low anodic degradation and a large amount of open porosity after sintering. The paper provides details of the fabrication of such powders. By comparison of laser and microwave heating with regard to energy efficiency, production rates and scale-up potential, the process is discussed from an economic point of view. The properties of the eutectic powders, the preparation of the electrodes and their electrochemical performance will be discussed focussing on effects particularly related to the lamellar microstructure of the material. This includes, e.g. the sintering behaviour. A retarded densification is observed for pellets pressed from eutectic powders ground to a grain size below 50 µm. Densification starts at 1250 - 1300°C in comparison to 1100°C using conventional powders. This demonstrates the high thermal stability of the powder. The amount of open porosity after sintering at 1400°C and reduction at 1000°C in H_2 is about 45% in comparison to 30% in conventional powders. Furthermore, the melt processing ensures the Ni particles to be jammed between the zirconia lamellae, resulting in a large amount of TPBs. This will result in low anodic overpotentials. Figure 1 shows the microstructure of a eutectic powder particle after annealing in Ar-5H_2 for 100h at 1000°C.

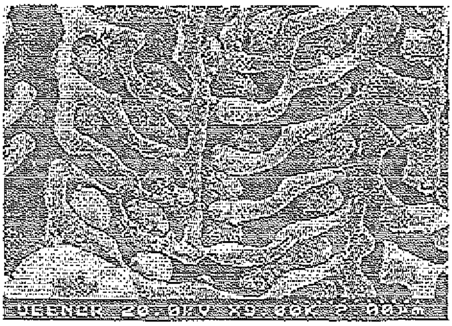

Figure 1: round Ni particles jammed between YSZ lamellae

Electrical Conductivity in $Ca_{1-x}Sr_xTi_{1-y}Fe_yO_{3-\delta}$ System

E.A. Mashkina, L.A. Dunyushkina, A.K. Demin, N.O. Esina

Institute of High Temperature Electrochemistry, Ural Division of RAS
20 S.Kovalevskoy Str., 620219 Ekaterinburg, Russia

Perovskite, $CaTiO_3$, is known to have mixed ionic and electronic conductivity and stable structure in reducing atmospheres [1]. That is why this material can be used as an oxygen permeated membrane for hydrogen production. For the ionic conductivity of $CaTiO_3$ is not high enough, in the present study, we investigated the influence of the substitution by Sr in A sites and by Fe in B sites on the conducting properties of the perovskite.

The samples of the system $Ca_{1-x}Sr_xTi_{1-y}Fe_yO_{3-\delta}$ ($x = 0, 0.5, 1$; $y = 0 - 0.6$) were synthesized by solid state reaction of the corresponding oxides or carbonates and attested by X-ray diffraction method. The total electrical conductivity was measured by the dc four-probe technique at various oxygen partial pressures. The oxygen partial pressure (Po_2) was set by an oxygen pump and controlled by an oxygen sensor.

For all compositions, the electrical conductivity dependencies on Po_2 confirm hole and electron conductivity at high and low Po_2, respectively, and a predominant ionic conductivity, independent on Po_2, in a wide region of intermediate Po_2. On the base of the temperature dependencies of the total conductivity at intermediate Po_2 the activation energies of the ionic conductivity were calculated.

The substitution by Fe in B sites results in increase of the ionic conductivity. However, in the system $SrTi_{1-y}Fe_yO_{3-\delta}$ the ionic conductivity rises monotonously with the iron concentration increase, while for the $CaTi_{1-y}Fe_yO_{3-\delta}$ and $Ca_{0.5}Sr_{0.5}Ti_{1-y}Fe_yO_{3-\delta}$ systems the ionic conductivity dependencies on y have a maximum at intermediate iron concentrations. The total substitution of Ca by Sr in A sites leads to increase of the ionic conductivity. The transport mechanism of charge carriers in the investigated system is discussed on the base of the conductivity and activation energy data.

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Oxygen Permeation in $La_{0.5}Sr_{0.5-x}Ca_xCoO_{3-\delta}$ (x=0-0.5)

R.P.Kononov, A.K. Demin, N.O. Esina
Institute of High Temperature Electrochemistry, Ural Division of RAS
20 S.Kovalevskoy Str., 620219 Ekaterinburg, Russia

Mixed ionic-electronic conductors based on perovskite-type oxides ABO_3 could be used as a material for oxygen separation membranes and in other applications. Substitution at A site by M^{2+} alkaline-earth element was found to enhance the oxygen transport properties by forming oxygen vacancies. The point defects model for this case does not reflect the difference in substitution by various divalent ions. The objective of our investigation was to reveal the effect of doping by various divalent ions on oxygen transport properties of $La_{0.5}Sr_{0.5-x}Ca_xCoO_{3-\delta}$ (x=0-0.5).

Perovskite type compositions $La_{0.5}Sr_{0.5-x}Ca_xCoO_{3-\delta}$ have been synthesized by a liquid precursor method and characterized by X-ray diffraction. The oxygen permeation measurements were performed in the temperature range 500-950^{0}C under various oxygen partial pressure gradients. This method allows to determine directly the steady flow of oxygen through the gas tight specimen at the constant temperature. It was shown that the oxygen permeability of $La_{0.5}Sr_{0.5-x}Ca_xCoO_{3-\delta}$ membranes increased significantly with increasing x. Using the permeation data the ionic conductivity of the samples was calculated. The $La_{0.5}Ca_{0.5}CoO_3$ has the maximum value of ionic conductivity. The activation energies of oxygen ion conductivity for different compositions are close and constitute about 90 kJ mol^{-1}. This fact indicates that the ionic transport mechanism is the same for all compositions. The ionic conductivity from one to two orders of magnitude higher than that of stabilized zirconia.

The total conductivity of the investigated system was measured by means of dc four-probe technique in the temperature range 400-1000^{0}C in air. On the base of these data and data on oxygen permeability the ionic transference numbers were calculated. Their values for all compositions are less than 0.005 over all temperature range.

THE HIGH-TEMPERATURE DEFECT STRUCTURE OF CdTe - COMPARISON BETWEEN THEORY AND EXPERIMENT

P.Fochuk, O.Panchuk, O.Korovyanko, P.Feychuk, I.Turkevych

Institute of Inorganic Chemistry, Chernivtsi University, 2, vul. Kotsiubinskoho, 274012
Chernivtsi, Ukraine, fax +380 (372) 55-18-05, e-mail: fochuk@chv.ukrpack.net

CdTe is one of the most important tellurides. Its single crystals are used for the fabrication of optoelectronic devices and radiation detectors. The electrical and optical properties are defined by the nature and concentration of native (NPD) and foreign (FPD) point defects. First Kr^ger and his collaborators proposed quasichemical reactions (QCDR) between defects in solids. The point defect spectrum is formed under high-temperature defect equilibrium conditions (HTDE) that is at ~ 300-10920C. As atomic point defects can not be observed directly, only electronic defects can be detected. Room or lower temperature free carrier density measurements are hard to be interpreted (NPD and uncontrolled impurities contents comparable). Thus high-temperature Hall effect experiments are the sole possibility to study the HTDE. Such models were elaborated by Kr^gerís school (Nobel, Chern) and presented in the form of diagrams. The last 10-20 years showed, that their models are in many cases not reliable (F.Smith, A.Martinaitis, O. Panchuk, P.Fochuk). Last new theoretical approaches for the construction of point defects diagrams were proposed (M.Berding, Q.Chen, M.Hillert, T.Anderson).

In this communication recent own and anotherís investigators experimental results are presented and compared with the existing models. It is shown that for the elaboration of reliable models sure free carrier density data versus not only stoichiometric relations, but also versus temperature and dopant contents are needed.

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High Temperature Materials in Molten Carbonate Fuel Cells

Peter Biedenkopf and Thomas Wochner[#]

Forschungszentrum Jülich GmbH
IWV 2 - Leo Brandt Straße
52425 Jülich
email: p.biedenkopf@fz-juelich.de

[#]MTU-Friedrichshafen GmbH
Abt. TQZ - Olgastraße 72
88045 Friedrichshafen
email: wochner@mtu-friedrichshafen.com

Molten Carbonate Fuel Cells (MCFC) are electrical energy devices which produce electrical energy by electrochemical oxidation of hydrogen at an average temperature of 650 °C. Inside the fuel cell methane (CH_4) is reformed to hydrogen according to Eqn.1 and hydrogen is electrochemically oxidized on the anode of the fuel cell:

$$CH_4 + 2H_2O = 4H_2 + CO_2 \qquad \text{(Eqn. 1)}$$

The electrolyte consists of different carbonate mixtures, whereby eutectic Li-K- or Li-Na-carbonate-mixtures are used. At operation temperature this melt is embedded in a ceramic, which consists of $LiAlO_2$ and Al_2O_3. The anode exists of Ni-Cr or Ni-Al alloys and the cathode exists of in situ oxidized NiO, which contains 2 mol.% of Li (lithiiated NiO), which has a very high electrical conductivity due to the defect electrons which are formed accorduing to Eqn.2.

$$Li_2CO_3 + 0{,}5\ O_2 = 2Li_{Ni}' + 2O_O^* + 2h^{\bullet} + CO_2 \qquad \text{(Eqn. 2)}$$

One main problem of the MCFC-technology is the corrosion of metallic materials, which are used as current collectors on the anode and cathode side and as separator plates between the cells. Corrosion scales which are formed on the cathodic current collector (CCC) minimize the effiency of the fuel cell due to increasing resistivity of the oxides and due to electrolyte loss caused by chromate formation in the oxidizing atmosphere. So the electrical conductivity of the corrosion scale should be as high as possible to prevent a power drop of the fuel cell. In the past, mostly austenitic FeCrNi-stainless steels were used as CCC and bipolar plate. Those alloys form a multilayered corrosion scale, in which a chromium rich oxide (spinels or $LiCrO_2$) is formed inside, whereas the outer layer consists of an iron rich layer ($LiFeO_2$ and $LiFe_5O_8$) [1-3].

We have investigated the corrosion behavior and the electrical conductivity of different Fe-Cr-alloys which also contains different amounts of Co and Mn. The investigations have shown, that the *inner corrosion layer limits mainly the conductivity of the total corrosion scale.* A high Cr-content above 20 wt.% (like in SS310S=1.4845) reduces the electrical conductivity significantly due to the formation of an Cr-rich $LiCrO_2$-layer in contact with the bulk material. A good electrical conductivity was observed on alloys which exhibit 16-18 wt.% of Cr (like in SS316L=1.4404), because these alloys forms well conductive spinel layers inside the corrosion scale. FeCrMn alloys form a three-layered corrosion scale with an Mn-rich oxide layer in contact with the molten carbonate after 5000 h of exposure. So the corrosion layer exists of a Cr-rich spinel layer inside overgrown by a $LiFeO_2$-layer and a Mn-rich layer on the top, which was identified by XRD as Li_2MnO_3. Co-containing alloys show also a three-layered corrosion scale with a $LiCoO_2$ layer on the surface. So alloys for use as CCC should embody 16-18 wt.% Cr, 8-15 wt.% of Ni and additionally 5-10 wt.% of Mn or Co, because these alloys forms well conductive, mixed spinel layers and exhibits a sufficient corrosion resistance.

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CATHODIC LOSSES IN SOLID OXIDE FUEL CELLS INVESTIGATED BY GEOMETRICALLY DEFINED MICROELECTRODES

V. Brichzin, J. Fleig, H.-U. Habermeier and J. Maier
Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

$La_{1-x}Sr_xMnO_3$ (LSM) has been receiving much attention for its possible use as the air electrode in solid oxide fuel cells (SOFCs) with yttria-stabilized zirconia (YSZ) as the electrolyte. Since the electrochemical performance of an SOFC is often determined by the oxygen reduction reaction that takes place at the cathode side, there has been much research into the oxygen reduction mechanism at the LSM electrode. However, for a better understanding of the oxygen reduction kinetics, a detailed knowledge of the geometry and morphology of the LSM/YSZ interface is required. Thus, several researchers have tried to better control the properties of this interface by either varying the sintering conditions to determine the electrode contact area or by using cone-shaped LSM electrodes which are pressed on the YSZ electrolyte. But, measurements with such microelectrodes are again subject to uncertainties since the resulting interfacial microstructure is still unclear.

In this contribution we present measurements on LSM micro-electrodes with a well-defined structure, geometry and contact area with the YSZ. By using photo-lithography on thin laser-ablated films (1000-4000 Å thick) of LSM on YSZ, we were able to create circular microelectrodes having ten distinct diameters between 10 and 200 μm. By the means of AC impedance spectroscopy and the I-U characteristics the relationship between electrochemical performance and electrode geometries has been studied. The micro-electrode experiments enabled us to investigate the dependence of the polarization resistance on the area of the two-phase boundary, the length of the three-phase boundary and the thickness of the LSM layer. These results will be discussed in terms of the oxygen reduction mechanism and its relationship to the geometrical parameters. Moreover, with these micro-electrode experiments the formation of the reaction layer $La_2Zr_2O_7$ (LZO), growing at the interface between stochiometric LSM and YSZ, can be measured very sensitively. The formation kinetics of such LZO interface layers and their importance for the electrochemical performance will be discussed.

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Thermodynamic Properties of $BaCe_{1-y}Eu_yO_{3-x}$ (y=0 – 0.1)

Toshihide TSUJI*, Hirokazu KURONO** and Yasuhisa YAMAMURA*
*Center for New Materials, Japan Advanced Institute of Science and Technology, Hokuriku, 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292 Japan
**Department of Nuclear Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan

High-temperature proton-conducting solids are useful materials for high-temperature fuel cells, hydrogen sensors, hydrogen gas separators, etc. Attractive candidates for protonic conductor at high temperature are the perovskite-type oxides such as $SrCeO_3$, $BaThO_3$ and $CaZrO_3$ where some trivalent cations are partially substituted for B site cations. Electrical properties of perovskite-type protonic conductor have been studied by many investigators, but the studies on their thermodynamic properties are lacking. In this paper, the thermodynamic properties of $BaCe_{1-y}Eu_yO_{3-x}$ (y=0–0.1) were studied by TG-DTA, TMA and high temperature X-ray diffraction measurements.

Analytical reagent grade $BaCO_3$, CeO_2 and Eu_2O_3 powders of the required proportion were mixed in an agate mortar, pressed into a cylindrical pellet and then calcined in a platinum crucible at 1523 K for 10 h in air. The calcined powders were mixed again and pressed into a cylindrical pellet at a pressure of 400 kg/cm^2. The pellet was then sintered at 1823 K for 10 h in air. TG-DTA, TMA and X-ray diffraction measurements were carried out for $BaCe_{1-y}Eu_yO_{3-x}$ (y = 0–0.1).

Analysis of X-ray powder diffraction patterns for $BaCe_{1-y}Eu_yO_{3-x}$ at room temperature showed the existence of a single phase with orthorhombic structure. The isomer shift(δ) for $BaCe_{0.9}Eu_{0.1}O_{3-x}$ sample(δ =0.91 mm/s relative to EuF_3) annealed in air at 1273 K which was determined by room temperature Moessbauer spectroscopy was close to that of a reference Eu^{3+} sample(δ =1.02 mm/s for Eu_2O_3) rather than that of a reference Eu^{2+} sample(δ =1.02 mm/s for $EuSO_4$), indicating that the europium ions are existed as the Eu(III) state. It has been found from TG-DTA measurement that doped samples of $BaCe_{1-y}Eu_yO_{3-x}$ were less stable than undoped $BaCeO_3$ in CO_2 atmosphere at constant temperature. At around 1100 K, both samples of $BaCe_{1-y}Eu_yO_{3-x}$ and $BaCeO_3$ showed a phase transition from tetragonal to cubic phase in high temperature X-ray diffraction measurement and the weight loss in TG measurement, probably due to oxygen evolution. Abnormal behavior was observed at around 1600 K for undoped $BaCeO_3$ in TMA measurement.

Phase Diagram Studies in the System La_2O_3-SrO-MgO-Ga_2O_3

Peter Majewski, Fritz Aldinger
Max-Planck-Institut für Metallforschung
Heisenbergstr. 5, 70569 Stuttgart, Germany

Sr and Mg substituted $LaGaO_3$ (LSGM) has been reported to have extraordinary oxygen ion conducting properties which is of great technological interest for solid electrolyte application in solid oxide fuel cells (SOFC). Recently, Huang et al. [1] have demonstrated that LSGM based SOFC have the potential to replace SOFC based on the solid electrolyte made of YSZ. This is because of the higher oxygen conducting properties of LSGM at temperatures of about 700 °C in air.

The knowledge of the phase diagram representing the thermodynamic equilibria of heterogeneous multi component systems are essential to understand the fundamental materials aspects underlying the preparation of single phase or controlled multi phase ceramics, and to understand the correlation between the microstructure of the prepared samples and the applied heat treatment.

LSGM has been found to be in equilibrium with Ga_2O_3, $La_2GaO_{4.5}$, $LaSrGa_3O_7$ (113 phase), MgO and a La-Mg-Ga-O compound at 1400 °C in air. The Sr and Mg solubility of LSGM appears to decrease with decreasing temperatures resulting in the formation of the 113 phase during annealing of LSGM at about 700 °C in air. Although the Sr as well as the Mg solubility of $LaGaO_3$ is low within the ternary systems La_2O_3-SrO-Ga_2O_3 and La_2O_3-MgO-Ga_2O_3, respectively, the solubility of the elements increases when Sr and Mg are alloyed simultaneously. This effect results in an extension of the homogeneity region of LSGM within the quaternary system La_2O_3-SrO-MgO-Ga_2O_3. In addition, Several new La-Sr-Ga-O and La-Mg-Ga-O compounds were found the crystal structure and chemistry of which will be presented.

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ELECTROCONDUCTIVITY OF $BaCe_{0.9}Nd_{0.1}O_{3-\alpha}$ IN (H_2+H_2O+Ar) GAS MIXTURES

A.V. Bannykh, B.L. Kuzin, V.P. Gorelov, S.M. Beresnev
Institute of High-Temperature Electrochemistry, Ural Division of Russian Academy of Sciences, Ekaterinburg, Russia

Solid electrolytes based on $BaCeO_3$ are thought to be a promising material for fuel cells, hydrogen pumps, sensors, etc. They possess both proton and oxygen conductivities at temperatures from 600 to 900 °C. This study deals with the effect of the H_2+H_2O+Ar mixture on electroconductivity of $BaCe_{0.9}Nd_{0.1}O_{3-\alpha}$ (BCN) and transfer numbers of oxygen ions (t_O) and protons (t_H). It was shown that BCN had purely ionic conductivity under the experimental conditions. At 600 °C the proton transfer number was close to unity. The values of t_H and t_O increased and decreased respectively with elevating temperature. When the temperature was constant, t_H and t_O were independent of the H_2+H_2O+Ar mixture composition, electrode polarizability, or direction (anodic or cathodic) of the polarizing current. Conductivity of BCN did not depend on P_{O_2} ($10^{-19} \div 10^{-26}$ atm) and P_{H_2} ($0.16 \div 0.99$ atm). When P_{H_2O} was increased ($0.003 \div 0.3$ atm), BCN conductivity was enhanced. In the first approximation this dependence can be written as $\sigma = K \cdot P^{n}_{H_2O}$. When the temperature was elevated from 600 to 900°C, the exponent n dropped from 0.20 to 0.03. Various models of defect formation in the given electrolytes were considered to explain the experimental findings.

ELECTRICAL, ELECTROCHEMICAL AND ISOTOPIC EXCHANGE MEASUREMENTS ON $LaGaO_3$-BASED CERAMICS

D. I. Bronin[a,b], B. L. Kuzin[a] V. P. Gorelov[a,b], E. Kh. Kurumchin[a], G. K. Vdovin[a],
Ju. V. Sokolova[a], M. Keppeler[b], H. Näfe[b], F. Aldinger[b]
[a] *Institute of High-Temperature Electrochemistry, S. Kovalevskoj 20,*
620219 Ekaterinburg, Russia
[b] *Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium,*
Heisenbergstraße 5, D-70569 Stuttgart, Germany

The present work aims at the characterization of the practically relevant electrical and electrochemical properties of differently doped $LaGaO_3$-based ceramics which are important for a potential application as solid electrolyte and electrodes for efficient electrochemical devices at intermediate temperatures (600 - 800 °C). For that purpose, perovskite materials with the total composition $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM) and $La_{1-x}Sr_xGa_{1-y-z}Mg_yCo_zO_{3-\delta}$ (LSGM-Co) were prepared by solid state technique.

The solubility limits of Sr and Mg in LSGM were estimated by electron microscopic analysis in view of the most relevant processing parameters. As a result, the formation of secondary phases is negligible if $x = y \leq 0.16$.

The electrical conductivity of LSGM and LSGM-Co was measured as a function of the oxygen partial pressure and temperature by means of ac- and dc-techniques. The data reveal that doping of LSGM with Co leads to an increase of the p-type conductivity.

By electrochemical and isotopic exchange measurements on both LSGM material and on an LSGM pellet whose surface was modified by Co-doping, it was shown that the oxygen exchange rate between the solids and the surrounding gas phase is much higher in the case of the modified electrolyte material. The temperature and oxygen pressure dependence of the exchange behaviour of the materials were characterized.

In order to evaluate the behaviour of LSGM in contact with typical electrode materials, impedance spectroscopy measurements on symmetrical cells were performed in various atmospheres with Pt, $La_{1-x}Sr_xCoO_{3-\delta}$ and Ni as electrodes. The electrochemical activity of $La_{1-x}Sr_xCoO_{3-\delta}$/LSGM and Ni/LSGM was found to be sufficiently high for a practical application in a solid oxide electrolyte fuel cell. Based on these results a single fuel cell with an LSGM electrolyte was constructed and tested using hydrogen as a fuel and air as an oxidant.

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DIFFERENCES IN THE BULK AND SUBSURFACE DIFFUSIVITIES OF OXYGEN IN COMPLEX OXIDES: ISOTOPIC EXCHANGE DATA

E. Kh. Kurumchin, V.I. Tsidilkovski, G.K. Vdovin, A.N. Ezin

Inst. of High-Temperature Electrochemistry RAS,
20 S.Kovalevskaya Str., 620219, Ekaterinburg, Russia

There is much evidence that subsurface regions in complex oxides can differ in the oxygen diffusivity from the bulk. Such differences may arise due to the peculiarities of chemical composition or defect structure of subsurface regions. Grain boundaries in ceramics can also act in some cases as a subsurface region.

Our recent developments [1] make it possible to detect the differences in the bulk and subsurface diffusivities of oxygen in oxides (simultaneously with the determination of the rates of the different types of the surface exchange) by the isotopic exchange method with gas phase analysis.

The peculiarities of oxygen diffusion in subsurface regions have been revealed by our approach in a number of oxides. For example in solid electrolytes $0.9ZrO_2+0.1Y_2O_3$ (single- and polycrystals) and $La_{0,88}Sr_{0,12}Ga_{0,82}Mg_{0,18}O_{3-x}$ (polycrystals) the subsurface diffusivities of oxygen are lower than bulk diffusivities calculated from the conductivity data. In $YBa_2Cu_3O_{6+x}$ dense ceramics diffusion of oxygen also follows a two-stage course and diffusivity at the first stage, probably due to the grain boundary diffusion, is at least an order higher than in the bulk.

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Vaporisation and Thermodynamics of the Ga_2O_3-La_2O_3 System by Knudsen Effusion Mass Spectrometry

*W. Kuncewicz-Kupczyk *, D. Kobertz, M. Miller *, and K. Hilpert*

Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
** On leave from: Wroclaw University of Technology, Wyb. St. Wyspianskiego 27, 50-370 Wroclaw*

Perovskites on the basis of $LaGaO_3$ are of interest as electrolyte for the development of Solid Oxide Fuel Cells (SOFC) which operate at low temperatures ($T<1073$ K). The vaporisation of the phases of the Ga_2O_3-La_2O_3 system was, therefore, investigated using Knudsen effusion mass spectrometry.

Mass spectra of the equilibrium vapours of the two phase samples composed of the phases $\{La_2O_3+La_4Ga_2O_9\}$, $\{La_4Ga_2O_9+LaGaO_3\}$, and $\{LaGaO_3+Ga_2O_3\}$ were measured in the temperature range of 1500 K – 1700 K. The following ions were detected in the mass spectra: O_2^+, Ga^+, GaO^+, Ga_2^+, Ga_2O^+, La^+, and LaO^+. The ions were formed by ionisation and fragmentation of the gaseous species O_2, Ga, GaO, Ga_2O, and LaO. The equilibrium partial pressures of the species were determined in the temperature range of investigations. By comparison of the partial pressures obtained over the two phase Ga_2O_3/La_2O_3 samples with those over pure $Ga_2O_3(s)$ the thermodynamic activity of Ga_2O_3 was evaluated using the reaction

$$\underline{Ga_2O_3} = Ga_2O(g) + O_2(g),$$

where $\underline{Ga_2O_3}$ means pure $Ga_2O_3(s)$ or the Ga_2O_3 component in the quasi binary phases $La_4Ga_2O_9$ or $LaGaO_3$. The thermodynamic activity of La_2O_3 resulted by Gibbs Duhem integration and by taking into account the phase diagram of the Ga_2O_3-La_2O_3 system. Gibbs energies of formation of the quasi binary compounds $LaGaO_3(s)$ and $La_4Ga_2O_9(s)$ were computed from the thermodynamic activities.

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VAPORIZATION STUDIES OF PURE CHROMIA AND CHROMIUM CONTAINING ALLOYS IN HUMID AIR

C. Gindorf and K. Hilpert,
Institute for Materials and Processes in Energy Systems, IWV 2,
Research Centre Jülich, 52425 Jülich, Germany

Chromium-based alloys as well as chromium-containing steels, used for high temperature applications, are protected from corrosion by a chromia scale. The chromium-based alloy Cr5Fe1Y_2O_3 (ODS) is considered as interconnect material for the planar solid oxide fuel cell (SOFC). The operating conditions on the cathode side of the SOFC are T = 950 °C, $p[H_2O] = 0.02$ bar and $p[O_2] = 0.21$ bar. Depending on temperature and the partial pressures of H_2O and O_2 volatile chromium species are formed by the Cr_2O_3 layer at the surface of the alloy (1, 2):

$$Cr_2O_3(s) + 1.5\ O_2(g) = 2\ CrO_3(g) \qquad [1]$$

$$Cr_2O_3(s) + 1.5\ O_2(g) + 2\ H_2O(g) = 2\ CrO_2(OH)_2(g) \qquad [2]$$

$$Cr_2O_3(s) + O_2(g) + H_2O(g) = 2\ CrO_2OH(g) \qquad [3]$$

The vaporization of gaseous chromium oxides and chromium oxihydroxides (equations 1-3) at the cathode side of the fuel cell can cause a rapid degradation of the electrical properties of an SOFC (1, 3). The reduction of volatile Cr(VI) species to solid Cr(III)oxide at the cathode/electrolyte/oxidant three phase boundary is considered to be the reason for the observed degradation of cell performance. Metallic interconnect materials are coated with ceramic layers (such as $La_{0.9}Sr_{0.1}CrO_3$) to reduce chromium vaporization in order to prevent the degradation processes (3). Also a decrease of the operating temperature is a suitable way of lowering the partial pressures of volatile Cr(VI) species.

In this paper the chromium vaporization rates from the surface of different chromium-containing alloys were determined by the use of a transpiration apparatus (4). The uncoated interconnect materials ODS alloy Cr5Fe1Y_2O_3 and steel X10CrAl 18 were investigated and the evaporation rates obtained were compared to those measured with coated samples. This non-equilibrium experiments were carried out under real cathodic SOFC conditions: T = 850 °C or 950 °C, gas flow rate v = 1.8 l/min, $p(O_2) = 0.21$ bar, and $p(H_2O) = 0.02$ bar. For the uncoated ODS sample (80x30x5 mm^3) a chromium vaporization rate of 8.6 µg/h was obtained for a temperature of 950 °C. ODS samples with a protective VPS coating ($La_{0.9}Sr_{0.1}CrO_3$) of 25 µm scale thickness showed under the same experimental conditions a 99 % lower chromium vaporization rate.

In addition to the transpiration experiments under non-equilibrium conditions, equilibrium studies were carried out using Cr_2O_3 samples. The vaporization of pure $Cr_2O_3(s)$ in air with different H_2O partial pressures (0.0007 bar - 0.3 bar) was determined at different temperatures between 400 °C and 950 °C by the transpiration method. For a decrease of the SOFC operation temperature from 950 °C to 850 °C a three times lower chromium transport rate was obtained.

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Interdiffusion between Electrode and Electrolyte Materials for Cathode Supported SOFC´s with MOD Thin Film Electrolytes

C. Argirusis°, M. Kilo°, A.C. Müller*, A. Weber*, G. Borchardt°, E. Ivers-Tiffée*
° TU Clausthal, Institut für Allgemeine Metallurgie
Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany
* Institut für Werkstoffe der Elektrotechnik IWE
Universität Karlsruhe (TH)
Adenauerring 20, D-76131 Karlsruhe, Germany

SOFC´s with an electrode supported thin film electrolyte (electrolyte thickness of about 5 to 10 µm) are a forward-looking alternative to electrolyte supported single cells because of the decreased electrolyte resistance. A cathode supported single cell, like the tubular cells used in the Westinghouse concept, is advantageous concerning the polarization losses of the cathode electrolyte interface, which precipitates a considerable part of the power losses in a conventional single cell. Therefore an economical operation of the cell at a decreased temperature (600 - 800 °C) should be possible.

One major problem of thin film electrolytes, the interdiffusion between electrode and electrolyte during production and operation of the cell, has been investigated by diffusion experiments: Diffusivities of several cationic impurities (Mn, La, Sr) into yttria stabilized zirconia (YSZ) relevant for the SOFC cathodes were measured using SIMS tracer techniques as a function of temperature (1100 to 1500 °C). Furthermore, first results for the interdiffusion of cations from the cathode (La, Sr, Mn, Co...) into the alternative electrolyte material LSGM (LSGM = (La,Sr)(Ga,Mg)O_3) are presented.

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Properties of Ni/YSZ Cermets depending on their Microstructure

A.C. Müller, B. Pei, A. Weber, E. Ivers-Tiffée
Institut für Werkstoffe der Elektrotechnik IWE
Universität Karlsruhe (TH)
D-76131 Karlsruhe, Germany

A cermet (ceramic metal composite) of Nickel and Yttria stabilized Zirconia (YSZ) is the most commonly used fuel electrode for Solid Oxide Fuel Cells (SOFC). Most SOFC single cells have a homogeneous single layer Ni/YSZ anode. However, these single cells show a high degradation due to an agglomeration of the Ni particles. Therefore it is necessary to develop a multilayer anode whose diverse layers will differ in their microstructure to fulfill the locally different requirements for SOFC anodes. Several samples of Ni/YSZ cermets with different Ni content, Ni grain size and YSZ grain size were prepared. The thermal expansion coefficient and the electrical conductivity of these samples was measured in air and hydrogen, respectively. The change of the sample length during several oxidation/reduction steps was studied by means of dilatometry. The kinetics of the oxidation and reduction of Ni/NiO within the cermet was investigated by Temperature Programmed Reduction (TPR). The goal of this investigations was to determine the influence of the grain size respectively the grain size ratio of the two components on the properties of the cermet.

Development of cathode supported SOFC´s with MOD Thin Film Electrolytes

U. Guntow°, A.C. Müller*, A. Weber*, G. Müller°, E. Ivers-Tiffée*
° Fraunhofer Institut für Silicatforschung ISC
Neunerplatz 2, D-97082 Würzburg, Germany
* Institut für Werkstoffe der Elektrotechnik IWE
Universität Karlsruhe (TH)
Adenauerring 20, D-76131 Karlsruhe, Germany

SOFC´s with an electrode supported thin film electrolyte (electrolyte thickness of about 5 to 10 µm) are a forward-looking alternative to electrolyte supported single cells because of the decreased electrolyte resistance. A cathode supported single cell, like the tubular cells used in the Westinghouse concept, is advantageous concerning the polarization losses of the cathode electrolyte interface, which precipitates a considerable part of the power losses in a conventional single cell. Therefore an economical operation of the cell at a decreased temperature (600 - 800 °C) should be possible.

Planar single cells (50 x 50 mm^2) have been prepared by depositing an YSZ electrolyte layer (YSZ: yttria stabilized zirconia) on a LSM cathode substrate (LSM: $La_{1-x}Sr_xMnO_3$) using MOD (metallo organic deposition), which is a cost effective technology compared to conventional thin film technologies like EVD or CVD. Thin film coatings with the desired target stoichiometry are produced from stable sols with a high solid yield by spin coating. This is followed by thermal treatment with a high heating rate. The interface properties i.e. the microstructure of the cathode electrolyte interface can be optimized by interlocking the thin film electrolyte with the cathode substrate resulting in an increased three phase boundary and an improved adhesion between cathode and electrolyte.

The single cells have been completed by screen printing a Ni/YSZ cermet anode onto the electrolyte layer. First results of electrical characterization of this type of cell will be shown.

A76

Phase stability, processing and electrical properties of (La,Sr)(Fe,Al)O_3 and (La,Sr)(Mn,Al)O_3 ceramics

D. Kolar, D. Kuščer, M. Hrovat and J. Holc
Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Perovskite type oxides (ABO_3) with rare earth elements on the A sites and transition metals on B sites, are well known for their refractory properties, catalytic activities and wide range of electrical properties. The (La,Sr)FeO_3 and (La,Sr)MnO_3 systems have been extensively studied because of their potential use as cathodes for soli[illegible]el cells. The significant limitation is the chemical reactivity between the [illegible] perovskites and the yttrium stabilised zirconia solid electrolyte at high temperatures. The partial exchange of iron or manganese with aluminium suppresses the reaction rate, however it also increases the specific resistivity and porosity of sintered ceramics. The electrical characteristics of doped La perovskites were evaluated as a function of phase compositions and processing conditions.

PROTON CONDUCTING ALKALINE EARTH ZIRCONATES AND TITANATES FOR HIGH-DRAIN ELECTROCHEMICAL APPLICATIONS

K.-D. Kreuer[1], A. Fuchs[1], St. Adams[2], W. Münch[1] and J. Maier[1]

1 Max-Planck-Institut für Festkörperforschung, Heisenbergstr.1, D-70569 Stuttgart
2 Georg-August-Universität Göttingen, Mineralogisch-Kristallographisches Institut
Goldschmidstr. 1, D-37077 Göttingen

Acceptor doped perovskite-type $BaZrO_3$- and $SrTiO_3$-based materials have the potential to combine high concentration and mobility of protonic defects ($OH_O^\bullet$) and thermodynamic phase stability [1], which makes them interesting candidates as alternative materials for oxide ion conductors (Y-stabilized zirconia, CeO_2- and $LaGaO_3$- based materials), which are currently being used as separator materials in high drain electrochemical cells such as solid oxide fuel cells (SOFC).

Since the A- and B-site occupation of these systems leave some space for a further optimization of the above properties, we have studied the effects of the kind and concentration of acceptor dopant in $BaZrO_3$, the effects of a mixed Zr/Ti occupancy on the B-site and mixed Sr/Ba occupancy on the A-site on the above properties.

While any structural and chemical pertubation originating from the B-site occupation leads to a significant reduction of the mobility of protonic defects, the A-site occupation can serve in the optimization of this parameter. The stability of protonic defects is found to essentially scale with the basicity of the lattice oxygen, which is influenced by both, A- and B-site occupation.

The interpretation of the results is backed up by quantum chemical calculations. The results of preliminary fuel cell tests are also presented.

1. K. D. Kreuer; Solid State Ionics (Proc. SSPC-9), in press (1999)

A 78

Proton Diffusion in Perovskite-type Oxides: Details of the Diffusion Mechanism Investigated by Quantum Chemical Simulations

W. Münch, K.-D. Kreuer, J. Maier, G. Seifert‡
Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1, 70569 Stuttgart, Germany
‡Universität Paderborn, FB 6 (Theoretical Physics)
Warburger Str. 100, D-33098 Paderborn, Germany

Protonic defects incorporated into perovskite-type oxides (ABO_3) can be the cause of substantial protonic conductivity. To investigate in detail the proton diffusion mechanism quantum chemical calculations have been carried out using $BaZrO_3$ and $SrTiO_3$ as model systems. Numerical results of both static and molecular dynamics calculations are presented. The numerical simulation results are found to be in reasonable agreement with experimental data. The impact of both structural changes and doping of the A- and B- sites on the protonic diffusion can be extracted from the numerical simulations.

A79

High Temperature Oxidation of Fe-Cr Steels with Regard to Their Application as Interconnectors for Solid Oxide Fuel Cells

K. Przybylski, T. Brylewski, J. Pra uch
Department of Solid State Chemistry, Faculty of Materials Science and Ceramics,
University of Mining and Metallurgy (AGH), al.Mickiewicza 30, 30-059 Cracow, Poland

Many efforts have been undertaken lately to apply the iron-base scalling-resistant steels in the construction of interconnectors for planar type solid oxide fuel cells (SOFC) operating at 1073 K in consideration of their advantages when compared with Ni or Co-based alloys and ceramic materials (e.g. (La,Sr)CrO3). The oxidation kinetics of Fe-25 wt.-% Cr and Fe-16 wt.-% Cr steels (Ni(1.0 %, Mn(0.4 %, Si(0.8 %) have been studied in H2/H2O gas mixture (pH2/pH2O=94/6) and air, corresponding to the anode and cathode operating conditions of SOFC, respectively, in the temperature range of 1073-1223 K for 75 up to 365 h. It has been observed that the oxide scale, composed mainly of Cr2O3, grows in accordance with a parabolic rate law. The dependence of the parabolic rate constant kp on temperature in H2/H2O gas mixtures obeys Arrheniusí equation: kp=6.0(10-3exp(-224 kJmol-1R-1T-1). The determined kp is independent of the oxygen partial pressure from 5.2(10-22 to 0.21 atm at temperatures 1073-1273 K, which implies that the growth rates of chromia scales on Fe-25Cr steel in the above mentioned atmospheres are comparable. To increase the insufficient electrical conductivity of the chromia scale forming on the steel at SOFC environment, calculated on the basis of kp and the specific resistance of Cr2O3 scale, the tested steel was covered with a conducting oxide layer of La0.6Sr0.4CoO3 using the screen printing method. The resistance of the coated Fe-25Cr steel did not exceed the resistance of the 0.5 cm thick (La,Sr)CrO3 ceramic interconnector in H2/H2O gas mixture and air at 1073 K, demonstrating its applicability as interconnector material for SOFC. The cross-sectional SEM-EDS investigations of the oxided steel covered with (La,Sr)CoO3 film revealed the formation of a thin and continuous enriched with Sr, layer of Cr2O3 at the metal/film interface. The detailed TEM-SAD observations of this chromia layer confirmed the segregation of Sr to Cr2O3 grain boundaries and formation of Sr-Cr oxide precipitates. Such oxide precipitates exhibit higher electrical conductivity than pure chromia scale and thus provide the electrical contacts between the interconnector material and the ceramic layer, creating the conditions for prolonged exploitation of SOFCís interconnectors.

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Synthesis and Physicochemical Properties of (La,Sr)CoO_3 for SOFC Application

K. Przybylski, T. Brylewski, J. Pra uch

Department of Solid State Chemistry, Faculty of Materials Science and Ceramics
Universdity of Minich and Metaalurgy (AGH), al. Mickiewicza 30, 30-059 Cracow, Poland

The paper presents the investigations concerning the synthesis, properties of L0.6Sr0.4CoO3 ceramic powders and its use for preparation of thick films on Fe-Cr steels for metallic interconnector application in SOFC. To prepare L0.6Sr0.4CoO3 micropowders with great homogeneity of the chemical and phase composition as well as the desirable narrow microparticle-size distribution a modified sol-gel method using the ethylene-diamine-tetra-acetic (EDTA) as a complexing agent of metal cations in a water solution was applied. The water solution of La, Sr and Co EDTA complexes obtained by mixing nitrate solutions of the above metals with 0.1 M EDTA under constant pH=8 was evaporated in vacuum at 383 K. Thermal decomposition of the resultant gel at 773 K for 1 h and its further calcination in air at 1273 K for 25 h yielded fine powders with the average grain diameter of about 0.5-1.5 (m (BET 5.6 m2/g) . The ASA and XRD analyses of the powders confirmed the desirable chemical and phase composition (indexed in a rhombohedral cell). The (LaSr)CoO3 thick films on Fe-Cr steel substrates were prepared using the screen-printing method and the paste obtained by mixing the La0.6Sr0.4CoO3 powder with 5 wt.-% solution of ethyl cellulose in terpineol. The films were deposited on the Fe-25 wt.-% Cr and Fe-16 wt.-% Cr steels (Ni(1.0 %, Mn(0.4 %, Si(0.8 %) using 100 mesh screen. The coated steels were oxidized in air at 1073 K for 144 h. The sintered films were 50-100 (m thick and were well adherent to the metal substrate. They contained small porosity. The XRD analysis indicates that thick film consists of almost single phase of La0.6Sr0.4CoO3. The average value of the electrical resistivity for coated Fe-25Cr steel with the thick layer measured during the oxidation process at 1073 K in air after 150 h was about 25 m(cm2, in comparison with 38 m(cm2 for a commercial ceramic (La,Sr)CrO3 interconnector, which indicates the possibility to apply this metal-ceramic composite material in SOFC construction.

A81

Defect Kinetics in Fayalite, Fe_2SiO_4

K. Ullrich and K. D. Becker
Institut für Physikalische und Theoretische Chemie,
TU Braunschweig, Hans-Sommer-Str. 10,
38106 Braunschweig, Germany

Olivines of the composition $(Fe_{0.1}Mg_{0.9})_2SiO_4$ are the most abundant minerals in the upper earth crust. Fayalite (Fe_2SiO_4) is the iron-rich end member of the solid solution series Fe_2SiO_4–Mg_2SiO_4, which crystallizes in the olivine structure with orthorhombic space group symmetry Pbnm. Transport of matter and charge in olivines depends on the orientation and also on the concentration of the point defecs.

Changes in the crystal composition of olivines cause variations of the point defect concentration. Electronic defects associated with the deviation from exact stoichiometry give rise to defect-induced optical absorption.

Polarized absorption specta of oriented fayalite single crystals have been measured *in-situ* at high temperature (1130°C) as a function of oxygen activity. The oxygen activity dependent defect spectra contribute to the understanding of the nature of the electronic defects. The results are discussed.

To study the orientation dependent kinetics of point defect re-equilibration in fayalite single crystals at high temperature, relaxation experiments with sudden changes in oxygen activity were carried out. Time dependent changes of absorbance, following isothermal jumps in oxygen activity within the stability field of fayalite, have been investigated.

The diffusion of defects in oriented single crystals was found to be anisotropic: diffusion is fastest in the c-direction and slowest in the a-direction. The ratio among the diffusion coefficients derived from these experiments for the three principle axes $D_a : D_b : D_c$ is approximately 1 : 6 : 13 at 1130°C. This behaviour is in reasonable agreement with results reported by Dieckmann and coworkers [1, 2].

In addition, diffusion along the three diffusion directions yields in different activation energies.

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A 82

Structure-property relations of perovskite-type oxides: Application of Goldschmidt's tolerance factor to highly defective oxides

Nikolai Trofimenko, Helmut Ullmann

Institute of Inorganic Chemistry, Technical University Dresden, 01062 Dresden

Abstract

Oxides of the perovskite-type structure are of interest as functional ceramics for high-temperature applications. Their properties can be modified in a wide range by doping on the A- and B-site, which changes the defect structure. Sometimes perowskite oxides exist in an extended range of defect concentration as monophase materials. The perovskite-structure is formed at a certain realtion of ionic radii, expressed by the tolerance factor of Goldschmidt

$$t = (r_A + r_O)/\sqrt{2}(r_B + r_O) = 0.75 \text{ to } 1.1$$

The undistorted cubic modification with best mobility of oxide ions is formed at t near 1 (1.04 to 0.95) [1]. Other authors [2,3] observed a strict correlation between Goldschmidts tolerance factor and the enthalpy of formation of the perovskite phases from the oxides, thus the tolerance factor could serve as an informal evaluation for the prediction of structure formation and properties. The problem is, that effective ionic radii are not available for highly defective oxides.

In this work an attempt is made for the calculation of effective ionic radii r_A, r_B and r_O for perovskites of high defect concentration on the basis of experimental data (O/M stoichiometry, lattice constants) on the defect structure of perovskite-type oxides. The results are demonstrated on the systeme $Ln^{3+}{}_{1-z}Sr^{2+}{}_{z}M^{3+}{}_{1-z}M^{4+}{}_{z}O_{3-\delta}$ (M = Mn, Fe, Co). Two defect models are analyzed: The oxygen excess region with a cationic vacancy structure and the oxygen substoichiometric region with an oxygen vacancy structure [4,5].

For verification of the suitability the t-factors calculated in this manner have to be correlated with experimental data on structure and properties (electrical conductivity, oxygen diffusion, catalytic activity ect.) of selected series of material compositions.

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COATING BY COPPER IN THE HIGH PRESSURE OF THE METALLOOXIDE HTSC CERAMICS SURFACE

Anatoliy D.Shevchenko

Institute of Metal Physics Ukrainian AS,
36 Vernadsky pr.,Kiev-252142,Ukraine

Technology of coating by copper in the high pressure (up to 5 GPa) conditions of the metallooxide HTSC ceramics surface has been developed with the help of high pressure techniques.The high pressure is produced by the hydraulic press of 2000 tons stress and high pressure solid-phase chambers of "toroid" type.

The copper coating on the surface of metallooxide HTSC ceramics is formed as a result of copper reducing reaction from copper oxide in the presence of carbon.Heating is realized under high pressure conditions in the presence of carbon in protective coating that excludes both loss of oxygen from HTSC ceramics and penetration of carbon into the volume of HTSC ceramics.From the HTSC ceramics samples with coating by copper of the metallooxide HTSC surface it is possible to produce long-dimensinal conductors,suitable for use at the liquid helium and nitrogen temperatures for special purpose.

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CVD OF $A^{III}B^{V}$: GAS PHASE CLUSTER FORMATION. STRUCTURES OF INTERMEDIATES AND THERMODYNAMICS OF ASSOCIATION PROCESSES

Alexey Y. Timoshkin
St. Petersburg state university, Department of Chemistry, University pr. 2, Old Petergof,
St.Petersburg, 198904 Russia; e-mail: alex@dux.ru

The Chemical Vapor Deposition process of group 13 metal pnictides from inorganic and organometallic precursors $R_3MYR'_3$ (M=Al,Ga; Y=N,P,As; R,R'=H,CH_3,Cl) has been considered. Geometries, relative energies, vibrational frequencies, and thermodynamic parameters are predicted for source precursors as well as their dissociation and association products employing B3LYP/DZP level of theory. In addition to widely accepted scheme of CVD as radical reactions on the surface, a new approach involving homogeneous gas phase cluster formation has been proposed and examined. The mechanism leading to carbon contamination of AlN and GaN via C-invaded clusters is also suggested and discussed.

Elimination of the first molecule RR' from $R_3MYR'_3$ leads to 3-coordinated species $R_2MYR'_2$ and strongly increases the metal-pnictide bond dissociation energy. For example dissociation enthalpy of Cl_2AlNH_2 is 420 kJ mol^{-1} compare to 149 kJ mol^{-1} for Cl_3AlNH_3. Therefore Cl_2AlNH_2, if formed, is expected to follow association processes rather than dissociation into radicals. In fact, for Cl_3AlNH_3 and Me_3GaNH_3 systems formation of gas phase aggregates has been experimentally evidenced. Theoretical modeling showed that association processes play key roles in the CVD of AlN from Cl_3AlNH_3 and important for Me_3GaNH_3 system. In opposite, for weak complexes M-Y dissociation energy remains the weakest even for 3-coordinated compounds (dissociation energies 51.5 and 249 kJ mol^{-1} for MeH_2GaAsH_2Me and MeHGaAsHMe, respectively) and for such systems formation of gas phase associates is thermodynamically unfavorable compare to generation of free radicals.

Therefore, the donor-acceptor bond strength in the source precursor may be used as a criterion in distinguishing between two principal CVD schemes. The role of radical reactions is extremely important for complexes with weak donor-acceptor bond ($\leq$ 60 kJ mol^{-1}), while for stronger bonded compounds ($\geq$ 80 kJ mol^{-1}) association processes are predominant at low temperature-high pressure conditions (including laser-assisted CVD).

Major processes during CVD of MY from $R_3MYR'_3$ molecular complexes:

	Dissociation pathway (weak adducts)	Association pathway (strong complexes)
1	$R_3MYR'_3 = MR_3 + YR'_3$	$R_3MYR'_3 = \frac{1}{n}(R_2MYR'_2)_n + RR'$ (n=2,3)
2	$R_3M = R_2M\cdot + R\cdot$; $YR_3' = YR_2'\cdot + R'\cdot$	$\frac{1}{n}(R_2MYR'_2)_n = \frac{1}{m}(R_2MYR'_2)_m + RR'$ (m=2-6)
3	Surface reactions to form MY	Cluster nucleation to form MY

High temperature transformation of sol-gel derived TiO_2 thin films into TiN films.

Y. DJAOUED[a], P.V. ASHRIT[b], R. TAJ[b], G. BADER[b], and T. VO-VAN[b].
[a]Secteur Sciences, Université de Moncton à Shippagan, Shippagan, N-B, Canada, E8S 1P6.
[b]Departement de physique, Université de Moncton, N-B, Canada, E1A 3E9.

Sol-gel chemistry has attracted wide spread interest of the materials science community due to its suitability for processing oxide materials in a wide variety of forms including monoliths, thin films, submicron spheres, fine powders, and high surface area xerogels and aerogels. Along side, there has also been an increasing interest in non-oxide ceramics such as silicon nitride and silicon carbide which possess high temperature strength, physical durability and corrosion-resistance. Among these, titanium nitride (TiN) is currently of great technological importance because of its extreme hardness and abrasion-resistance comparable to diamond, its high melting temperature (2950° C), high chemical durability, gold colour and metallic conduction. In the present study, sol-gel derived titanium dioxide (TiO_2) thin films on fused quartz substrates were converted to titanium nitride films by heating in controlled flow of NH_3 gas. First, we have studied TiO_2 thin films prepared by the sol-gel method using polymeric solutions formed upon hydrolysis-condensation of titanium alkoxide. These films were then deposited on quartz substrates by dip coating method. The effects of solution content (type of titanium alkoxide, type of solvent, equivalent oxide concentration, type of deflocculant reagent, $[H_2O] / [Ti(OR)_4]$ ratio), gas moisture during deposition and heat treatment temperature on the film properties were studied in detail. Then, the mechanisms of nitridation of these sol-gel derived TiO_2 films which was found to commence around a temperature of 700°C has also been investigated in depth to optimize their optical and electrical properties. The complete transformation seems to take place at temperatures higher than 1000° C, where brownish-golden TiN films were achieved. The various relevant properties of the TiN films were investigated by spectrophotometry, ellipsometry, electrochemistry, X-ray diffraction, and atomic force microscopy. This method provides a simple and economical means of depositing TiN hard coatings on different sized and shaped substrates with the capability of fabrication on a large scale.

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PREPARATION OF FERROELECTRIC FILMS BY PYROLYSIS OF METAL-ORGANIC SOLUTIONS APPLIED TO SUBSTRATES

O.V.Demirskaya, T.P.Rebrova, V.L.Cherginets and T.S.Teplitskaya
Institute for Single Crystals, Lenin ave.,60, Kharkov,310001, Ukraine

Ferroelectric films are widely used in different branches of industry and science. The main problem of obtaining devices for microelectronic purposes is connected with the creation of structure "metal–ferroelectric film–metal" over semiconductor material (Si) with the high quality of the interface boundaries.

The proposed way of obtaining ferroelectric films over different substrates is based on the method of coating application using solution metal organic precursors similar to developed in our recent works for HTSC materials.

Every applied layer of the citrate solution of metals-components of oxide film was subjected to the next annealing procedure: t_1=80-100°C, τ_1=10-30 sec; t_2=350-420°C, τ_2=30-60 sec; t_3=550-600°C, τ_3=30-60 sec to obtain perovskite in the oxide layer without additional annealing. The good wetting of substrates was provided by varying of composition of mixed solvent "ethylene glycole - alcohol" that allowed to avoid the stage of substrate rotation. Such a multistaged treatment provided easy evaporation of the solvent (t_1), decomposition of metal organic compounds (t_2) at the maintaining adhesion of the film to the substrate and uniform thickness of layer applied.

$PbTi_{0.5}Zr_{0.5}O_3$(PZT), films over Ni, Pt, Si(111), α-Al_2O_3, $SrTiO_3$, substrates have been obtained and studied by X-ray phase analysis. Electrophysical characteristics of structures obtained are dependent on electrode materials(Al, Ag, Pt, Au) and conditions of its application.

DEPOSITION OF PROTECTIVE NiAl coatings ON THE INTERNAL SURFACES OF tubes

C. Metz*, G. Wahl*, P. Bianchi**, M. Innocenti***, J.-P. Hirvonen****

* Institut für Oberflächentechnik und Plasmatechnische Werkstoffentwicklung, Technische Universität Braunschweig, Bienroder Weg 53, 38108 Braunschweig, Germany
** ENEL, Via Rubattino, 54, 20134 Milano, Italy
*** Nuovo Pignone, Via F. Matteucci 2, 50127 Firenze, Italy.
**** JRC Petten, Institute for Advanced Materials, 1755 ZG Petten, The Netherlands

Abstract: The oxidation resistance of nickel based superalloys used for high temperature components in gas turbine engines can be increased by the formation of NiAl layers. In the last years turbine blades constructed with cooling channels to lower the superalloy material temperature require the development of an uniform coating process to protect the internal surface. Therefore an investigation of the coating of Inconel 600 tubes with an internal diameter of 1 mm and a total length of 350 mm were made. After aluminising the internal surfaces with an AlCl3/Al CVD process a heat treatment was performed under vacuum. The thickness and the composition homogeneity of the resulting NiAl layers along the length of the tubes were examined before and after the heat treatment. These layer thickness were determined by optical and scanning electron microscopy. The layer composition was measured by EDS X-ray microanalysis. The homogeneity of the resulted coatings was correlated to the deposition parameters like the deposition temperature and deposition time and carrier gas.

Theoretical investigation of laser oxides film deposition

Danilenko V.M., Zaslavsky A.M.
IPM NASU, Kyiv, Ukraine

The models of laser evaporation and film deposition processes were constructed for conditions of real deposition chamber environment. The whole scenarium of deposition was devided into 4 stages - heating of target, transport to base layer, condensation of vapor and crystallization of film. The corresponding mathematical problems were solved by means of numerical and simulation methods on personal computer. Programs were written in object programming style with dynamical distribution of memory in Borland Pascal 6.0 language. For laser impulses of 1 ms duration temperature distribution in target corresponds to the Lambert law modified by heat transport phenomena. In vapour phase we obtain velosity distribution law of oxide molecules for target surface temperature conditions. On the base layer surface liquid film condensation gives some definite temperature depending of vapour pressure in chamber. After film deposition abrupt fall of surface temperature gives very high temp of cooling, which depend on initial base layer temperature To, but after some depth under surface we have also region of initial heating. For several To cynetic of crystal-lisation were simulated on PC with 100x200x200 cub. nm film specimen. Two To regions were revealed (from 300 K to 1000-1100 K and above that), in which Arrenius law have different parameters - one for higher To corresponds to prevaluation of grain grow processes and another - at low To on grain nucleation. Mean grain size values correspond to the experimental ones relatively well.

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“Unusual phases” and “unusual” phase equilibria in epitaxial thin oxide films

A.R.Kaul*, O.Yu.Gorbenko*, I.E.Graboy*, S.V.Samoylenkov*, M.A.Novojilov*, A.A.Bosak*,
H.W.Zandbergen† and G. Wahl††

**Department of Chemistry, Moscow State University, 119899 Moscow, Russia*

† National Centre for HREM, Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands

††IOPW, TU Braunschweig, Bienroder Weg 53, 38108 Braunschweig, Germany

An analysis of authors experience in high temperature MOCVD of thin films of multicomponent oxide compounds in respect of epitaxial phase stabilization phenomena will be given in the paper.

The phase relations of complex oxide systems in thin epitaxial films may differ from those known for bulk materials. In this study, the formation of nonequilibrium-in-bulk phases and the appearance of new phase relations has been observed in off-stoichiometric epitaxial films of high Tc superconductors (001) $RBa_2Cu_3O_{7-\delta}$. It was supposed, that the formation of coherent interfaces, which are inherent in epitaxial film growth, enables stabilization of otherwise non-equilibrium phases. Thus, epitaxial growth of a new barium cuprate, $BaCu_3O_4$, has been demonstrated in (001)$RBa_2Cu_3O_{7-\delta}$ films and on (001) single crystalline perovskite substrates using XRD and HREM of the cross-sectioned films with electron nano-diffraction. Also, in the epitaxial matrices of (001)$RBa_2Cu_3O_{7-\delta}$ the inclusions of well oriented R_2CuO_4 (R = Gd), R_2O_3 (R = Lu, Ho, Y), $R_2Cu_2O_5$ (R = Lu), Ba_2CuO_3 nanoparticles were observed depending on the films' stoichiometry but no evidence was found for the presence of structuraly non-coherent R_2BaCuO_5 or $BaCuO_2$, which are the equilibrium phases with bulk $RBa_2Cu_3O_{-\delta}$. It is concluded that the formation of coherent or semi-coherent interfaces between embedded inclusions and the surrounding matrix is critical for a stabilization of otherwise non-equilibrium oxide phases in epitaxial films.

Analogously, the formation of epitaxial $NdMn_7O_{12}$ layer at the surface of (001) oriented film of CMR-material $Nd_{1-x}MnO_{3+\delta}$ was reproducibly observed while in the policrystalline samples of corresponding composition the extra manganese oxide exists as Mn_3O_4 hausmannite equilibrium phase. $NdMn_7O_{12}$ phase in bulk was known to be stable only at high pressure.

For R_2O_3-NiO-O_2 systems it was shown that perovskite phases $RNiO_3$ form as thin epitaxial films at T-Po_2 conditions which are definitely beyond the thermodynamic stability limits for bulk samples. The effect is due to stabilizing contribution of coherent film/substrate interface lowering free energy of the system respectively to policrystalline state.

The thermodynamic and kinetic respects of these phenomena, their relation to Dankov-Van der Merve principle, as well as the role of interface mismatch and volumetric factors are discussed. It is concluded that thin film growth techniques provide a powerful tool for synthesis of unstable-in-bulk compounds in an epitaxial state and search for new complex oxides.

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PULSE LASER DEPOSITION OF BORON CARBIDE THIN FILMS

Sulkhan Shalamberidze
The Institute of Stable Isotopes
21, Kavtaradze str., Tbilisi, 380086, GEORGIA

Boron carbide thin films have been produced by a method of pulse laser deposition. Depending on the experimental conditions, amorphous, polycrystalline and oriented films have been deposited on NaCl, silicon and sapphire substrates. The investigations of the composition and energy characteristics of the laser plasma have been carried out. The experiments showed that the plasma formed during boron carbide film production by a method of pulse laser deposition contained up to 20 % of ions with the mean energy 120 eV. A considerable decrease of the temperature of crystalline growth was observed in films deposited on the NaCl substrate from a target of boron carbide enriched in a 10B isotope up to 90 %.

Over a temperature range 270-700 K, the specific electric conductivity of boron carbide crystalline films shows temperature dependence by law (~ T-1exp(-Ea/kT) where the activation energy Ea equals respectively 0.056 eV and 0.085 eV for polycrystalline and oriented films. The specific electric conductivity of boron carbide amorphous films varied by law ln(~ T-1/4 over the whole range of temperatures under investigation (4.2-700 K). The same relation is characteristic of crystalline samples at low temperatures (<200 K).

The boron carbide films are irradiated both by thermal and fast neutrons in a nuclear reactor. The electric conductivity of the samples is measured during the irradiation.

Poster Presentations B

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Intrinsic Diffusivities and Diffusion Paths in Fe-Ni-Cu Alloys

R. Bachorczyk, M. Danielewski and T. Walec
University of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Cracow, Poland

The limited amount of data concerning transport properties of multicomponent systems is due to lack of reliable analytical and numerical methods for the calculation of intrinsic diffusivities and tracer diffusion coefficients and especially their concentration dependence. The generalized Darken model of interdiffusion offers new numerical methods and allows for a complete quantitative description of complex diffusional transport process and for unlimited number of elements. It allows for calculating diffusion paths and other diffusion related effects when interdiffusion coefficients as well as intrinsic diffusivities are concentration dependent.

The Fe-Ni-Cu system was chosen because of a wide range of compositions that can be chosen as starting materials in the diffusion couples and because its thermodynamic properties are fairly well known. Beside, the solid solutions in this system are not ideal and consequently intrinsic diffusivities are not constant. The driving force for diffusion in such ternary system is gradient of the chemical potential. It can be calculated from the concentration profile and using the known thermodynamical data of the system. Consequently the diffusional flux can be expressed as a function of the concentration gradient, thermodynamical therm and of the mobility. Such formulae is self-consistent with used by us generalized Darkens' model of interdiffusion.

The Fe-Ni-Cu system offers numerous possibilities in studying and modelling of diffusion paths in single phase areas and across $\alpha|\beta$ interface. The interdiffusion was studied using the diffusional couple technique and for different temperatures. The computed diffusional paths show good agreement with the measured ones. The method of calculation the intrinsic diffusivities will be presented and diffusivities of Fe, Ni and Cu as a function of temperature will be shown. The transport properties of Fe-Ni-Cu system are consistent with the literature data for Cu-Ni and Fe-Ni systems.

B2

Interdiffusion in Multicomponent Solid Solutions: from Diffusional Structures in Alloys to Hyperbolic Diffusion

M. Danielewski[1], W. Krzyżański[2] and R. Bachorczyk[1]

University of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Cracow, Poland
University at Buffalo, 410 Capen Hall, Buffalo, NY 14260, USA

The Darken's concept of separation of diffusional and drift flows, i.e., the postulate that the total mass flow is a sum of diffusion flux and translation only, is applied for the general case of diffusional transport in r-component solid solutions (process defined as interdiffusion in one dimensional mixture). The equations of mass conservation (continuity equations), the appropriate expressions describing the fluxes (drift flux and diffusional flux) allow a complete quantitative description of diffusional transport process to be formulated.

It has been shown that when certain regularity assumptions (concerning initial data) and, a quantitative condition (concerning the diffusion coefficients and providing a parabolic type of the final equation) are fulfilled, then there exists the unique solution of the interdiffusion problem (i.e., the generalized Darken model of interdiffusion). An effective algebraic criterion allows to determine the type of particular problem. In general "the regular diffusion" (parabolic type equation) and "accelerated diffusion" (hyperbolic type equation) can result from the presented model. Theoretical criterion for diffusional structures formation in ternary and higher alloys will be presented.

We will demonstrate computer simulations of several interdiffusion processes and present experimental data. Namely, the interdiffusion in quaternary (Fe-Mn-Cr-Si), and higher alloys and for „parabolic" type of the process will be shown. The development of the „up-hill diffusion" (diffusional structures) in the multicomponent alloys will be presented and compared with experimental data (single phase Co-Fe-Ni alloy and multiphase Ni-Al-Pt-Cr-Co superalloy). We will show computer simulations of interdiffusion in multilayred systems as well as experimental data for couples of finite thickness (Co-Fe-Ni alloys). Finally simulation of „hyperbolic" diffusion in arbitrary ternary alloy will be demonstrated.

B3

Interdiffusion in Oxidised Ternary and Higher Alloys

M. Danielewski[1], R. Filipek[1], M. Hetmańczyk[2], J. Łaskawiec[2], A. Milewska[1] and A. Rakowska[1]

[1]University of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Cracow, Poland
[2]Silesian Polytechnic, ul. Krasińskiego 8, 40-017 Katowice, Poland

In spite of the importance of the multicomponent alloys and coatings there is a gap between understanding their properties and actual level of commercial applications (e.g., very little is known on the relation between alloy transport properties and mechanism of its high temperature oxidation). The reduction of this gap may help in development of a wide group of new materials. The commercial alloys are usually a multicomponent and multiphase. In this work we will show the recent progress in understanding the diffusion processes in single phase solid solutions and in particular the diffusion in an reacting, e.g., oxidized, multicomponent alloy. We restrict our treatment to single phase alloys only and will show its capability in future applications (multiphase alloys).

The oxidation of single-phase binary and higher alloy usually does not follow the parabolic rate law. Even relatively simple process of the selective oxidation of binary alloy consists of the initial incubation period followed by the quasi-steady-state conditions (parabolic kinetics). Thus, variable boundary conditions and resulting complex kinetics must be taken into account in quantitative modelling of the rate of the reaction. Moreover under such conditions an alloy|scale interface may become morphologically unstable and develop non-planar geometry.

The generalized Darken model of interdiffusion enables to obtain an exact expression for the evolution of component distributions in open systems, e.g., as a result of the thermo-chemical treatment and/or oxidation. The proposed here boundary conditions allow to study the evolution of the alloy composition as a result of its reaction with a surrounding environment, e.g., allow to predict the concentration profiles of all elements beneath the growing sulphide scale. Finally, the rate of the reaction can be calculated on the base of Wagner's theory.

We will show the evolution of the Fe-Mn-Cr alloy composition because of its sulphidation and will compare computed results with experimental ones. The studies of interdiffusion in Fe-Cr-Mn diffusional couples allow to calculate intrinsic diffusivities of all alloy components. An agreement between the computed and experimental results suggests that the postulated boundary conditions correctly describe the transport process in open system and in particular allow for the modelling of the alloy oxidation process.

B4

Intrinsic Diffusivities and Thermal Stability of Multicomponent Coatings

R. Bachorczyk[1], M. Danielewski[1], S. Datta[2], R. Filipek[1] and A. Rakowska[1]

[1] University of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Cracow, Poland
[2] University of Northumbria at Newcastle, UK

The incorporation of Pt in Ni aluminide coatings is known to be effective in improving the high temperature thermal stability and the corrosion resistance of superalloys. We have studied interdiffusion in Pt modified β-NiAl coatings on MAR M002. Such an coating-alloy system consists of nine metals (> 1% at) and several microalloying elements. In order to effectively use the generalized Darken model of interdiffusion the number of components was reduced ($r = 5$). Moreover the Morral's method of average concentrations was used in order to anticipate the multiphase structure of both the superalloy and of the diffusional barrier. The relaxed boundary and arbitrary initial conditions allowed to compute interdiffusion in as-received commercially coated samples.

The Pt effect on the diffusion of elements in Pt modified β-NiAl on MAR M002 superalloy has been studied at 1073, 1173, 1273 and 1373 K and for various annealing times. The measured concentration profiles in the coating/alloy system were used to compute the effective intrinsic diffusivities of Pt, Al, Ni, Co and Cr as a function of temperature. This information will be used to predict the extent of interdiffusion and the evolution of the distribution of the elements occurring after long annealing times. Comparison of the measured and calculated distribution of elements in such multiphase system will be shown. Such computations allow to predict thermal stability of the coating-alloy system.

The results obtained will be used to verify the generalized Darken's model. Further progress is possible upon using the equations describing the interdiffusion processes in the general case where the components' diffusivities vary with composition. Such formulae will be presented and simulation of the interdiffusion in a quaternary alloy system showing variable intrinsic diffusivities of all elements will be shown.

DIFFUSION COEFFICIENTS OF REFRACTORY AND RARE-EARTH METAL COMPLEXES IN MOLTEN SALTS

S.A. Kuznetsov[1,a] and M. Gaune-Escard[2]

[1]Institute of Chemistry Kola Science Centre RAS, 184200 Apatity, Murmansk region, Russia
[2]IUSTI-CNRS UMR 6595, University of Provence, F-13453 Marseille Cedex 13, France

Electrolysis of molten salts is a promising method for production of advanced materials from refractory and rare-earth metals and their alloys. Diffusion coefficients (*D*) are an important transport characteristic of molten salts, and in the present study we determined the influence of melt composition on the diffusion coefficients of rare-earth complexes.

In the present study numerous values of diffusion coefficients for refractory and rare-earth metal halide complexes in alkali chloride melts were determined. The majority of these data was obtained by chronopotentiometry and linear sweep voltammetry methods. Influence of the composition of the first coordination sphere of the complex and the alkali metal cation comprising the second coordination sphere as well as the oxidation state of the central atom on the values of *D* were determined. It was found that the diffusion coefficients decrease when going from chloride complexes to fluoride to oxofluoride complexes. A decrease in *D* was also found when the alkali metal chloride melt was changed, i.e. as the cation composition of the second coordination sphere changes from Li to Cs. Thus increased basicity of the melt decreases the value of the diffusion coefficient. It was also found that *D* decreased with increasing oxidation state of the central atom and ionic moment of the diffusing species

In this study model equations were considered for the calculation of *D*, and their agreement with experimental data discussed.

Difficulties in the determination of diffusion coefficients of rare-earth metal complexes in the melts were found to be due to the closeness of the potential discharge of rare-earth (M) and alkali (Me) metals, appearance of the electronic conductivity according to the reaction :

$$3Me + MCl_3 \Leftrightarrow 3MeCl + M \qquad (1)$$

Reaction (1) results in decreasing of the concentration of the rare-earth metal in the vicinity of the electrode compared to its higher concentration in the bulk of the melt.

[a] *SAK is grateful for support of this study under a NATO grant.*

B6

Interdiffusion Paths in the Diffusion Couple Y-Al_2O_3

M. Ohtsuka[*], R. Cremer, E. Zimmermann, Dieter Neuschütz

Lehrstuhl für Theoretische Hüttenkunde
Rheinisch-Westfälische Technische Hochschule Aachen
D-52056 Aachen, Germany

The interface reactions in the diffusion couple Y-Al_2O_3 have been investigated at 1273, 1373, and 1473 K. The diffusion couples were prepared by depositing 4 µm of Y on Al_2O_3 substrates by means of magnetron sputtering and a subsequent annealing for up to 100 h under inert atmosphere. Grazing incidence X-ray diffraction (GID) and energy dispersive X-ray analysis (EDX) served to analyze the phases formed by diffusion processes in the reaction zone. The sequence of phases and their time scale was determined.

Thermochemical considerations have been applied to describe the interdiffusion and formation of interface phases in the diffusion couple Y-Al_2O_3 for the case of a thin Y layer on an Al_2O_3 substrate. With relevant thermochemical calculations, possible diffusion paths are discussed and their progress simulated.

[*] Guest scientist from: Institute for Advanced Materials Processing, Tohoku University, Sendai, Japan

PROPERTIES OF TiC AT HIGH TEMPERATURES

Ewa Maria Fryt

Department of Solid State Chemistry
University of Mining and Metallurgy
Al. Mickiewicza 30, 30-059 Kraków, POLAND

In highly defective solids in which concentration of point defects is higher than 0.1 % interactions between defects become important and have influence on many macroscopic structure sensitive properties of these compounds.

For description of interactions between defects in highly defective solids it is necessary to introduce new terms in diffusion theory characterizing interaction energy between defects especially for dependence of defect concentration on activity of compound components and temperature and as a result on the effective activation energy of diffusion defects, atoms or ions and all related on its macroscopic properties of compounds. The above mentioned function is characteristic for a crystallographic lattice of a given compound, different types of defects and their concentrations, attractive or repulsive interactions between defects and for a given diffusion mechanism.

This approach will be discussed and as an example interpretation of properties of TiC at high temperatures will be given.

TiC can be regarded as a model system for transition metal monocarbides. This group of compounds is interesting and very important for technology because of its good mechanical properties, very high hardness, good thermal and electrical conductivities, very high melting temperatures over 3000 K and usually very wide phase field and very high concentration of defects reaching maximum values even over 50%. Many structure sensitive macroscopic properties of carbides have unusual character of its dependencies on concentration of defects, passing by extremum. At so high concentration of defects, interactions between defects are expected and its influence on macroscopic structure sensitive properties of these compounds.

The influence of strong repulsive interactions between carbon vacancies and stronger than that attractive interactions between titanium atoms, on many macroscopic properties of TiC will be shown. The free energy of these interactions, the enthalpy of the mobility of carbon vacancies in TiC has been determined and discussed in this work giving new informations on the mechanism of carbon diffusion in crystallographic lattice of TiC.

B 8

Formation of Equilibrium Thermal Defects and Chemical Diffusion in Fe-Al-Alloys

Theodor Hehenkamp, Raimund Kerl and Bernd Köhler
Institut für Materialphysik der Universität
Hospitalstr. 3 - 7, 37073 Göttingen

Absolute concentrations of vacancy like thermal defects in Fe-Al-alloys have been measured between 25 and 50 at % Al by means of differential dilatometry and positron annihilation techniques, which have been calibrated by quantitative determination of positron trapping rates. Defect formation can be grouped into two categories by their effective enthalpy and entropy of formation as well as by the effective formation volumes obtained from the pressure dependence of positron annihilation. At lower Al concentration up to 35 at % the defects appear to be single vacancies, whereas at higher Al concentrations aggregates as triple defects or divacancies have to be considered. In this context the B 2 - phase field has to be split into several regions, separated by higher order transitions, the limits of which can be rather precisely determined and resemble to a great extent dividing lines given already earlier by Köster and Gödecke. As a result Arrhenius plots in regions of more than 35 at % Al show sudden breaks followed by small slopes, which give the appearance of rather low effective formation energies of only 0,3 to 0,5 eV, which are unphysical. These can be shown to be the result of temperature dependent changes in local order. Whereas vacancy concentration generally increases with the Al content, chemical diffusion does not. Here the mobility plays the significant role, which has been studied in detail by following the annihilation of quenched - in vacancies by positron annihilation. Mobility is slowed down substantially with increasing Al concentration being closely related to the substructure in B 2 already mentioned. Also the thermodynamic factor plays a substantial role but introduces also some uncertainty. From the Kirkendall effect it becomes apparent, that the intrinsic diffusion coefficients of the two species Fe and Al are almost of the same magnitude, Al being always a little faster. In order to determine the Kirkendall effect precisely enough the partial molar volumes at diffusion temperatures have to be known quite well since these alloys produce a marker shift not only by different diffusion fluxes of the constituents but also by volume contraction.

B9

Demixing of oxides in a temperature gradient

Hauke Timm and Jürgen Janek

Institut für Physikalische Chemie und Elektrochemie
Universität Hannover
Callinstr. 3-3A, 30167 Hannover, Germany

e-mail: janek@mbox.pci.uni-hannover.de

Multicomponent compounds with variable composition demix kinetically under the influence of a temperature gradient at high temperatures. We investigated (a) the behaviour of the nonstoichiometric binary chalcogenides $Ag_{2+\delta}S$ and $Ag_{2+\delta}Se$ and of the binary oxide $Cu_{2-\delta}O$ (cuprite) in a defined temperature gradient by applying electrochemical techniques. Data for the so-called heat of transport of the mobile metal component are determined and discussed in relation to the corresponding defect structure. The influence of internal defect equilibria on the measurable heat of transport is exemplified.

We also studied (b) the demixing of the oxide solid solution (Co,Mg)O in a defined temperature gradient, and the difference of the heats of transport of the mobile metal components is evaluated. In addition, we observed pore migration under the influence of the temperature gradient, leading to severe changes of the microstructure of the ceramic material. This pore migration can be understood as a consequence of an internal shortcircuit for matter transport and is also formally treated.

All observations are described within the framework of linear irreversible thermodynamics and point defect thermodynamics.

B 10

Synthesis and Crystal Structure of New Oxides in CaO-Y_2O_3-SiO_2 System.

Toru Nagasawa, Hisanori Yamane and Masahiko Shimada

Institute for Advanced Materials Processing, Tohoku University, Sendai, 980-8577, Japan.

In CaO-Y_2O_3-SiO_2 ternary system, apatite-type structure compounds of $Ca_2Y_8Si_6O_{26}$ and $Ca_3Y_6Si_6O_{24}$ have been reported. It was pointed out that the real chemical composition of apatite-type compounds had not been established. The preparation of $Ca_2Y_2Si_2O_9$ was carried out, but the crystallographic data has not been reported yet. Since silicates have many isomorphs and form many complicated structures, new compounds having new structures would be expected in this multicomponent system. The present study attempt to prepare the compounds in CaO-Y_2O_3-SiO_2 ternary system and make clear their crystal structures.

$CaCO_3$, Y_2O_3 and SiO_2 powders were used as starting materials. These powders were weighed and mixed with ethanol. After drying and pelletizing, the samples were fabricated at 1700K for 72 h in air. The fabricated pellets were ground into powders and characterized by X-ray diffraction. The crystal structures of the products were refined by Rietveld analysis. Single crystal of $Ca_3Y_2Si_3O_{12}$ and $Ca_3Y_2Si_6O_{18}$ were prepared from melts by slow cooling. The crystal structures were analyzed by single crystal X-ray diffraction.

In CaO-Y_2O_3-SiO_2 ternary system, the compounds prepared at 1700K in air were $Ca_2Y_8Si_6O_{26}$ (apatite-type structure), $Ca_2Y_2Si_2O_9$(cuspidine-type structure), $Ca_3Y_2Si_3O_{12}$ (silico-carnotite-type structure) and $Ca_3Y_2Si_6O_{18}$(new structure).

A single phase having an apatite-type structure was prepared at $Ca_2Y_8Si_6O_{26}$. This phase is hexagonal, a=b=0.9341(1), c=0.6788(1)nm. The sample of $Ca_3Y_6Si_6O_{24}$ which was reported as apatite-type compound composed of two phases, $Ca_2Y_8Si_6O_{26}$ and $CaSiO_3$. It was confirmed that $Ca_2Y_2Si_2O_9$ had a cuspidine-type structure (monoclinic $P2_1/c$) and its lattice parameters were determined to be a=0.74468(3), b=1.049240(3), c=1.09661(4)nm, β=110.170(3)° .

The new compound, $Ca_3Y_2Si_3O_{12}$ is isostructual with silico-carnotite ($Ca_5(PO_4)_2SiO_4$). $Ca_3Y_2Si_3O_{12}$ is orthorhombic with space group $P\,nma$, a=0.65574(2), b=1.56066(3), c=1.00399(2)nm. The new compound, $Ca_3Y_2Si_6O_{18}$ (monoclinic $C\,2/c$, a=1.33422(5), b=0.77320(3), c=1.47959(6)nm, β=90.263(3)°) composed of ternary SiO_4 rings. Ca and Y atoms are in between the layers of ternary SiO_4 rings(Si_3O_9).

High-temperature oxide ceramic materials, containing heterovalent magnetic atoms

Bobrysheva N., Chezhina N., Osmolovski M.
Dept. of Chemistry, St.Petersburg State University, Universitetskii pr.2,
St.Petersburg, Petrodvorets, Russia, 198904.

The latest achievements in the field of oxide ceramics with unusual electrical and magnetic properties are associated with oxide systems of various structure containing paramagnetic atoms in heterovalent states. The problems of optimizing their properties (superconducting, magnetoresisting and so on) lay in the control over the synthesis , equilibration, and proper characterization by the composition, structure, dispersity of composite oxide materials. The variation of paramagnetic atom states in the high-temperature oxide ceramics with corundum or perovskite-like structures can be attained by a selected composition of diamagnetic components necessary to form a specified structure (for example $La_{1.85}Sr_{0.15}Cu_yAl_{1-y}O_4$ or $La_{0.67}Sr_{0.33}MnO_3$). Moreover, among other factors the dispersity of the initial compounds and of the resulting materials can be of great importance for the properties of the ceramics as a whole. This can be explicitly illustrated by the ceramics with corundum structure. Solid solutions of paramagnetic oxides in isomorphous diamagnetic matrices appear to be an efficient instrument for studying the effects of variations in the diamagnetic component composition on the electrical, magnetic and other physico-chemical properties of the oxide ceramics.

The study of the conditions of synthesis and the examination of temperature and concentration dependencies of magnetic characteristics of wide series of solid solutions, containing heterovalent atoms of copper, manganese and iron in the K_2NiF_4 and perovskite type oxides revealed that the microstructure of the ceramics under study are characterized by the formation of nano-size clusters. These very clusters determine the properties of the ceramics as a whole:

i. Superconducting properties of $La_{1.85}Sr(Ba)_{0.15}CuO_4$ and their solid solutions in $LaSr(Ba)AlO_4$ correlate with the existence of clusters, containing heterovalent copper atoms and oxygen, in the lattice where the character of interatomic interactions changes with temperature.

ii. Interatomic interactions in manganites depend on the type of the clusters and can be ferro- and antiferromagnetic.

Interatomic interactions in the complex oxides appear to depend on the composition of the diamagnetic sublattice.

iii. Interatomic interactions in corundums depend also on the type and size of the clusters, the latter being determined by the prehystory of a sample.

The obtained regularities can provide an instrument for selecting the starting components and the diamagnetic lattice composition to obtain particular electrical and magnetic behavior.

B 12

High Temperature Synthesis of $Sr_3[BP_3O_{12}]$

A.Baykal*, M.Kızılyallı* and R.Kniep**
*Department of Chemistry Middle East Technical University, Ankara - TURKEY
**Technische Hochschule Dramstadt, Eduard-Zintl Institute, Anorganische Chemie II, Hochschule str., 10, D-64289, Dramstadt, GERMANY.

Preparation of $Ba_3[BP_3O_{12}]$ was done previously by our group through the solid state reaction of $BaCO_3$ + H_3BO_3 + $(NH_4)_2HPO_4$ with the molar ratio of 2:1:3 at 1300 °C. Using excess amount of $(NH_4)_2HPO_4$ as a flux enabled the growth of single crystals together with $Ba_2P_2O_7$ in the powder form. In this study we tried to prepare the Sr compound using $SrCO_3$ + B_2O_3 + P_2O_5 with the ratio of 6:1:3 as given by the following equation:

$$6SrCO_3 + B_2O_3 + 3P_2O_5 \text{ --------> } 2Sr[BP_3O_{12}] + 6CO_2$$

The reactants were heat treated at 600, 700, 800, 900, 1000, 1200 °C for different time intervals. At 1000 °C, $2Sr[BP_3O_{12}]$ was obtained but in addition to this compound, $Sr_2P_2O_7$ and $SrBPO_5$ was also formed. But all the peaks found in the X-ray powder pattern was indexed with the given unit cell parameters. This proved that some of the d-spacings of $Sr_2P_2O_7$ and $SrBPO_5$ are same with that of $Sr[BP_3O_{12}]$.

The whole pattern was indexed in the orthorhombic system with the unit cell parameters of (after refinement process) a=22.25(4), b=14.32(2), c=7.11(1) Å with the space group of Ibca (No:73), Z=8. The X-ray powder and IR data of the product was reported the first time in this work.

B 13

Ternary Phases in the System Al/C/N

Falko D. Meyer and Harald Hillebrecht
Universität Bayreuth, Lehrstuhl ACI, Universitätsstr. 30, 95447 Bayreuth, Germany

Ternary phases in the system Al/C/N are known as high-temperature materials and high temperature semiconductors. Despite their promising properties, their structural chemistry is not very well established.

The aim of our investigation was the synthesis of pure compounds in the system Al/C/N and their characterisation.

The compounds were synthesized by high-temperature synthesis in a high-temperature furnance with graphite heater. The phases were characterized by the means of X-ray single crystal structure analysis, X-ray powder diffraction, FT-IR- and FT-Raman-spectroscopy, UV/Vis and DTA measurements. Quantitive analysis was done by WDX measurements.

The crystal structure of the Al5C3N is isotypic to that of (-Al4SiC4 showing a strong relation to the structure of aluminium carbide (Al4C3) and to the wurtzite structure type (AlN). Aluminium is tetrahedrally coordinated, the AlC4-tetrahedra are linked through shared corners and edges to layers. These layers are connected through AlN4-tetrahedra. Al5C3N is build during processing of AlN ceramic in the presence of carbon.

Powder samples of Al6C3N2 and Al7C3N3 could be obtained. Single crystal growth of these two phases is under current investigation.

Al4C3 shows a high solubility for nitrogen. Up to ca. 10% of the carbon atoms can be substituted by nitrogen. A change in colour (from yellow to brown) and a decrease of the chemical stability against hydrolysis results. By substitution of carbon by nitrogen, Al4C3 becomes an insulator with a larger bandgap.

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Ternary Phases in the System Al/Si/C

Falko D. Meyer and Harald Hillebrecht
Universität Bayreuth, Lehrstuhl ACI, Universitätsstr. 30, 95447 Bayreuth, Germany

Composite materials made of an aluminium based matrix reinforced with silicon carbide fibres are promising candidates for "high fitech" applications. In view of optimizing the production of such materials by melt infiltration, a general study of the reactivity of liquid aluminium towards silicon carbide has been undertaken.
The aim of the investigation was the synthesis of pure compounds in the system Al/Si/C and their characterization.

The compounds were synthesized in molten aluminium, by solid-state reactions and by high-temperature synthesis. The preparative work was done in a high-temperature furnace with graphite heater. The phases were characterized by the means of X-ray single crystal structure analyses, X-ray powder diffraction, FT-IR- and FT-Raman-spectroscopy, UV/Vis and DTA measurements. Quantitive analysis was done by WDX measurements.

The crystal structure of (-Al4SiC4 is isotypic to Al5C3N showing a strong relation to the structure of aluminium carbide (Al4C3) and to the wurtzite structure type (SiC). Aluminium is tetrahedral coordinated, the AlC4-tetrahedra are linked through shared corners and edges to layers. These layers are connected through SiC4-tetrahedra. (-Al4SiC4 is formed during sintering of SiC with Al as sintering aid.

Ruby coloured single crystals of Al8SiC7 could be obtained by high temperature synthesis. The crystal structure is under current investigation. Vibrational spectra show a close relation to the structure of (-Al4SiC4.

From Al4Si2C5 only powder samples could be obtained, single crystal growth of Al4Si2C5 is under current investigation.

Novel precursor derived boron containing silicon carbonitrides: The influence of boron on high temperature stability.

Peter Duerichen, Ralf Riedel
Material Sciences Department, Technical University of Darmstadt
Petersenstr. 23, 64287 Darmstadt, Germany

In recent years there has been considerable interest in preparing mixed ceramic phases containing Si, N, C, and B since the addition of B was reported to improve the thermal and mechanical properties of such multielement compounds over those of the binary Si_3N_4, SiC or also ternary SiCN materials.

There are different pathways of how to prepare such materials which are pursued by several groups like the copolymerization of chloroboranes and chlorosilanes with ammonia or amines, the polymerization of borazines or the hydroboration of polyvinylsilazanes to name just a few.

We are currently investigating the transformation of polymers obtained by ammonolysis of hydroborated vinylsilanes into amorphous SiBCN ceramics. These ceramic materials turned out to have excellent thermomechanical properties like no weigth loss up to 2000°C as well as a reduced tendency to crystallize [1]. The "glass transition" was found to occur at a temperature as high as 1600°C. Moreover the ceramics exhibit a nearly zero long term creep and show outstanding resistance to oxidation [2]. Together with the low density SiBCN ceramics seem to be very prospective candidates for different kinds of high temperature applications.

For the further development of these materials it is of great importance to learn more about the structural and microstructural changes which occur during polymer to ceramic transformation and during application at elevated temperatures.

The amount of boron as well as the environment of boron has turned out to play an importand role for the stabilty of the ceramics which is until now not fully understood. Therefore we have synthesized precursor molecules with different Si to B ratios and boron environments. After pyrolysis the Si/B ratio of the precursors is then found unaltered in the ceramics. This approach allows for a correlation of the Si/B- ratio and the molecular structure with the resultant properties. The influence of boron can only be clarified by a cooperation with other groups utilizing preparation of novel precursor molecules together with different types of analytical tools like simultaneous thermoanalysis (STA), solid state NMR, X-ray scattering or transmission electron microscopy.

Here we want to present some recent results in the Si/B/C/N system obtained within this field of interdisciplinary research.

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B 16

NANOSTRUCTURED HIGH MELTING POINT COMPOUND-BASED MATERIALS: SYNTHESIS AND PROPERTIES

R.A. Andrievski
Institute of Problems of Chemical Physics, Russian Academy of Sciences
Chernogolovka, Moscow Region, 142432 RUSSIA

High-melting point compounds (HMPC) are carbides, borides, oxides, nitrides and other those with the melting point above 2000°C (or even 2500°C). The most of HMPC may be described as advanced ceramics and their promising properties and wide application are well known. However, the information on HMPC properties in nanocrystalline state which is normally characterized by the grain size below 100 nm is not so comprehensive. In recent times nanostructured materials have attracted attention because of the hope to realize unique physical, mechanical, and chemical properties and in this connection analysis situation regarding to HMPC seems to be interesting and important.

Different methods of nanostructured material preparation such as powder technology, controlled crystallization from amorphous state, films and coating technology as applied to HMPC are discussed and compared in detail. The difficulties to obtain dense and nanocrystalline specimens are pointed. High-energy consolidation methods such as high-pressure sintering, shock compaction, electro-discharge compaction, magnetron sputtering and so on seem to be the most effective.

Physical-chemical and mechanical properties of nanostructured HMPC are generalized. Size effects in the thermodynamic and structural properties of these materials are discussed in detail. The effect of transition into nanocrystalline state on the phase diagram is illustrated by the example of the TiN-TiB_2 system.

STEADY-STATE CHEMICAL VAPOR TRANSPORT IN CLOSED AMPOULE REACTOR: MEASURED AND PREDICTED GROWTH RATES OF $SnS_2(s)$ CRYSTALS

By

Y.K. Rao and C.H. Raeder, Department of Materials Science & Engineering
302k Roberts Hall, Box 352120, University of Washington
Seattle, Washington 98195, U.S.A.

Abstract

Chemical vapor transport (CVT) is a reliable technique for preparing single crystals of oxides, sulfides, and other compounds of specified stoichiometry. The crystal growth is usually conducted in a closed ampoule-reactor-configuration under isobaric conditions. The gaseous 'transport agent' or 'solvent', typically a halogen (Cl_2, I_2) or a hydrogen-halide (HCl, HI), converts the solid-precursor, placed in the hot source-zone (at temperature T_s) of the reactor, to gaseous products which are then 'transported' to the cooler deposition-zone (at temperature T_d) wherein the reverse reactions occur producing crystals of desired orientation. The mass-transport mechanisms may include thermal convection, thermal diffusion and Stefan flow in addition to the ordinary (molecular) diffusion. It will be noted that the concentration-gradients which act as the 'driving forces' for the mass-transport of species in the gas-phase are the result of a carefully maintained temperature-gradient along the length of the reactor.

For the purposes of quantitative description of the CVT process, the ampoule-reactor may be regarded as consisting of three zones — source, connecting, and deposition (H. Schäfer, Chemical Transport Reactions, 1964, Academic Press, New York); in the two end-zones, the concentrations of the respective gas species are established by gas-solid reactions; as nucleation and reaction steps occur rapidly at elevated temperatures, a state of virtual ('near') equilibrium is expected to prevail in the end-zones, with gas-phase mass-transport between them limiting the rate of the overall crystal-growth process. For the chemical vapor deposition of $SnS_2(s)$ in a 15-cm long X 15-mm inner diameter ampoule-reactor, using a stannic iodide (SnI_4) solvent, with $T_s \rightarrow T_d$ = 798K → 723K, the partial pressures of eleven gaseous species (SnI_4, SnI_2, I_2, S_2, S_3, S_4, S_5, S_6, S_7, S_8 and I) are computed in both the source (at T_s) and deposition (at T_d) zones by combining the Iterative equilibrium constant method with the Stefan-Maxwell diffusion formalism; from these data, the diffusion-limited rates are computed for the respective species and the net rate of growth of the crystalline-phase (Sn/S = 0.5 molar ratio) is determined for a specified initial amount of the solvent (SnI_4). The convection effects are negligible in the pressure range investigated (85 Pa to 20 kPa). The computed rates are compared to the reported measurements of H. Wiedemeier and F.J. Csillag (Journal of Crystal Growth, 1979, vol. 46, 189-197).

B 18

THE STRUCTURE AND HIGH-TEMPERATURE MECHANICAL PROPERTIES FOR TERNARY ALLOYS BASED ON CHROMIUM

O.A. Bilous, M.P. Burka, N.I. Tsyganenko, L.V. Artyukh,
A.A. Bondar, T.Ya. Velikanova, O.I. Dovbenko

I.M. Frantsevich Institute for Problems of Materials Science,
National Academy of Science of the Ukraine
3 Krzhizhanovsky Str., 252180 Kyiv, Ukraine

The investigations of phase diagrams for the $Cr\text{-}M_{IV,V}\text{-}C$ systems together with the high resistance of chromium to oxidation are the foundation for the development of high-temperature eutectic alloys based on chromium.

About 35 compositions of Cr-Ti-C, Cr-Zr-C, Cr-Nb-C and Cr-Ta-C alloys were melted in the regions of quazibinary eutectics. The structures of the alloys under investigation were hypo-, hyper- and pure eutectic. It was shown that eutectic alloys are in effect a "natural composite" - chromium matrix which is reinforced by dispersed fibres (TiC, ZrC, and NbC) or mixture of fibres and right-angle plates (TaC). The high dispersivity of the hardening phase, its significant volume content, from 11 % for (Cr)+(ZrC) to 19 % for (Cr) + (NbC), as well as high thermal stability of eutectic structures formed at crystallization, allows to obtain good high-temperature mechanical properties. Thus at 1000°C the level of hardness for (Cr)+(TaC) alloy is found to be 1860 MPa, for (Cr)+(NbC) is 1560 MPa and for (Cr)+(TiC) is 1360 MPa. The obtained results are shown the good outlook for the eutectic alloys based on chromium as high-temperature materials.

Formation and Irradiation-Induced Optical Absoption in MeV Boron Ion Implanted $KNbO_3$ Optical Waveguides

Xia Zonghuang[1], Li Yan[1] ,Shen Dingyu[1] ,Wang Xuemei[1] ,Zhao Qiang[1] , Ma Xiaoyan[2], Shen Dezhong[2], Wang Kuiru[3]

[1]Department of Technical Physics, Institute of Heavy Ion Physics, Beijing 100871,P.R.China

[2]Research Institute of Synthetic Crystals, Post Box 733, Beijing 100018,P.R.China

[3]Department of Applied Science and Technology, Beijing Universuty of Post and Communications, Beijing 100088,P.R.China

Potassium niobate ($KNbO_3$) shows excellent electro-optic, nonlinear optical and photorefractive properties which make it a potential candidate for integrated and nonlinear optical applications.

We have demostrated the fabrication of nonleaky buried waveguides in $KNbO_3$ by 6.0 Mev B ion implantation with 1×10^{15} cm^{-2} dose. The microstructure of MeV B ion implanted $KNbO_3$ waveduides has been investigated by high-resolution TEM. The crystalline structure and the lattice damage in the waveguiging region, and the boundary of the waveguide have been observed.

In addtion, the irradiation-induced optical absorption of ion implanted $KNbO_3$ waveguides has been evaluated experimentally in dependence on wavelength, irradiation dose.

B20

Crystal Growth and Structure of Nb_5Sn_2Ga by Metal Tin Solutions and Properties of the Crystals

Shigeru Okada[a], Kunio Kudou[b], Toetsu Shishido[c] and Tsuguo Fukuda[c]

[a] *Faculty of Engineering, Kokushikan University, 4-28-1 Setagaya, Setagaya,*
Tokyo 154-8515 Japan
[b] *Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi,*
Kanagawa, Yokohama 221-8790 Japan
[c] *Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba,*
Sendai 980-0812 Japan

In a previous paper we reported the existence of a new ternary intermetallic compound Nb_5Sn_2Ga[1]). The purpose of this paper is to clarify the conditions for growing relatively large crystals of Nb_5Sn_2Ga in high temperature tin solutions by a self flux method using Nb and Ga metals as starting materials under a He gas. Crystallographic data, crystal size, crystal morphology, chemical analysis, superconductivity, electric property and microhardness of the crystals were measured, and oxidation at high temperature in air was studied. Nb and Ga were weighed in atomic ratios of 1.5:1, 2:1, 3:1, 4:1 and 6:1. Tin was added to these mixtures at a weight ratio of 5:1. The mixture of these three elements was placed in a Al_2O_3 crucible and heated under a He gas. The temperature of the furnace was raised at a rate of 400℃h^{-1} up to 1400℃ and kept for 10 h, and then slowly cooled down at a rate of 1℃h^{-1} to 1000℃. Then the furnace was rapidly cooled down to room temperature. The crystals were separated by dissolving Sn in dilute HCl for 4 days. The ternary single crystals Nb_5Sn_2Ga were obtained in the form of prismatic shape extending in the [001] direction, and with (100) and (110) faces. The compound shows superconductivity at T_c=1.75 K and ΔT_c=140 mK. The resistivity at room temperature is in the range of 253-277 $\mu\Omega$ cm and is metallic. The Vickers microhardness value on (001) plane and (100) or (110) planes of crystals is in the range of 8.5-10.1 GPa. The Oxidation of Nb_5Sn_2Ga crystal starts at about 562℃. The final oxidation products were NbO_2, $Nb_{12}O_{29}$, Nb_2O_5, SnO_2 and Ga_2O_3.

1) T.Shishido, K.Ukei, N.Toyota et al., J. Cryst. Growth, 96 (1989) 1.

Experimental Investigations and Thermodynamic Prediction of the Formation of Complex Precipitates During High Temperature Processing of High Strength Low Alloy Steels

S.Ranganathan, National Metallurgical Laboratory, Jamshedpur 831 007, India
A.N. Bhagat, and O.N. Mohanty, Tata Steel, Jamshedpur 831 001, India

High strength low alloy (HSLA) steels are extensively used for applications where the strength-to-weight ratio is a crucial design factor. These alloys contain various alloying elements such as Ti,Nb,V,Cr,Mn,Mo. These form complex precipitates during the processing of these alloys at high temperatures. The chemistry and size of these precipitates have to be carefully controlled to achieve the desired properties in application. These precipitates have a complex chemistry containing more than one alloying element in the anionic as well as the cationic sub-lattice of the precipitate. For appropriate design of the alloy, it is necessary to predict the precipitate chemistry at different alloy compositions and temperatures. In addition to these complex precipitates, copper which is added as an alloying element to these steels, also precipitates strengthening the steel thereby. Therefore, the environment in which the precipitates are formed also changes during the processing of the steel.

Electrical resistivity of HSLA steels were measured at different temperatures s a function of time. From the measured resistivity, the kinetics of precipitation of copper from the matrix was explored. The precipitation kinetics was satisfactorily described by a Jhonson-Mehl type of equation.

The technique of successive partial equilibration was employed to predict the chemistry of the precipitate and that of the matrix at different temperatures and different alloy compositions. The predictions were consistent with experimental results. This technique which has been recently introduced is versatile and easy to apply. This is based on the thermodynamic principle that the equilibrium state of a system is independent of the path followed to reach that. This technique overcomes the limitations experienced in the prediction of chemistry of complex precipitates using the conventional methods.

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A study of SiC fabrication from rice husk and its ash by Acheson Process

P.Saewong, K.Sujirote and P. Thavorniti
National Metal and Materials Technology Center
NSTDA Building, Rama VI Road, Bangkok 10400, Thailand

Rice is a main agricultural product of Thailand. The rice as well as its husk is produced in abundance each year. In spite of that, utilisation of the rice husk has not been fully identified although some has already been employed as, e.g., an insulating material for low temperature applications and a fuel for power plants. Additionally, a large amount of its ash from incomplete combustion in the power plants still remains unexploited. It has been reported that the husk, which is rich of silica and carbon, may be pyrolytically heat treated to form SiC in a controlled atmosphere. Thus the large quantity of the unexploited husk and its ash which silica and some carbon still remain could be an alternative raw material, rather than silicon and coke, for SiC fabrication in the countries where the rice husk is plentiful. However, massive production by the pyrolytic route is not favorable. Other possible method, e.g. Acheson method, which a large amount of the raw material is heated directly in an electrical furnace, is therefore considered.

The aim of this study is to determine the feasibility of SiC production in a lab scale from the rice husk and its ash with various carbon contents. The raw materials is heated up in a electric furnace to the same temperature range of 1350-1500(C as done for the pyrolytic process described in the previous paper [Sujirote et al]. However the holding time is varied from 0.5-6 hrs. The initial amount of the carbon of the raw material necessary for the SiC formation by this process will be established. Characterisation of the material heated will be carried out regarding carbon and silica residues and SiC contents. The microstructure will be observed comparing with those produced from the pyrolytic method in the previous paper. The electric energy consumed through the production process will be also analysed.

SOME PECULIARITIES OF SINTERING OF BORON AND BORON CARBIDE

S. Shalamberidze*, G. Kalandadze*, A. Eristavi*, A. Peikrishvili**

* The Institute of Stable Isotopes, 21, Kavtaradze str., Tbilisi, 380086, GEORGIA
** The Institute of Mining Mechanics, 6, Mindeli str., Tbilisi, 380086, GEORGIA

The results on the investigation of compacting kinetics in boron and boron carbide sintering are presented. With the example of boron carbide, the influence of the granulometric composition on the temperature dependence of compaction, on reaching a high final density, on gaining a homogeneous grain composition, in compacting was shown. The results on the α-rhombohedral boron usage in reacting sintering for boron carbide production are given.

With the example of boron, maximum compacting at the final sintering stage was reached as the process was managed under the conditions providing the successive phase transitions $\mathbf{B}_{\text{amorph.}} \rightarrow \mathbf{B}_{\alpha} \rightarrow \mathbf{B}_{\beta}$. The results on sintering of boron and boron carbide samples preliminarily compacted by explosive compression were considered. Prior to sintering no cohesion occurred on the contact surfaces of the crystals, however a high density was reached. Subsequent sintering at relatively lower temperatures is sufficient for the submicropores to disappear and for intercrystalline cohesion to occur. Explosive pressing – sintering gave an opportunity for producing the samples of the low-temperature forms of boron – the amorphous and α-rhombohedral ones. Some thermal and electrical properties of sintered boron carbide samples are presented.

B 24

Undercooling Phenomenon and Rapid Solidification of Liquid Metals and Alloys

Binbo Wei
P.O.Box 624, Northwestern Polytechnical University, Xian 710072, P.R. China

Undercooling phenomena take place when liquid metals and alloys are subject to such extreme conditions as containerless processing and high superheating. Its physical mechanism is that metallic melts can be cooled down to a temperature well below their equilibrium solidification point and maintain a metastable liquid state , if their heterogeneous nuclei are eliminated efficiently. Once a liquid is undercooled, its thermal physical properties will exhibit a significant change as compared with their values above freezing temperature. Its crystallization process is characterized by rapid solidification, which brings in the formation of a great series of novel microstructure morphologies. As an extreme case, some alloy melts can be continuously undercooled to the glassy state via amorphous solidification.

The objective of the present paper is to provide a comprehensive review on undercooling investigations and give a concise summary of the author's recent research results. Emphases are put on the high undercooling and rapid solidification of liquid Fe, Co, Cu and their alloys. Electromagnetic levitation, drop tube processing and glass fluxing methods are applied to achieve large undercooling up to 371 K. The specific heat of undercooled liquid metals is measured and used to calculate other thermodynamic properties such as Gibbs free energy change during rapid solidification. The high undercooling condition includes the rapid growth of dendrites and eutectics and results in a drastic grain refinement effect and an anomalous eutectic structure. In addition, Zr based alloy are successfully undercooled to form a kind of bulk metallic glass.

B25

DESCRIPTION OF Al,Si ORDERING IN CORDIERITE USING THE CLUSTER VARIATION METHOD.

Victor L. Vinograd, Andrew Putnis, and Herbert Kroll. Institute of Mineralogy, University of Münster, Corrensstrasse 24, D-48149 Münster, Germany.

Cordierite, $Mg_2Al_4Si_5O_{18}$, is an important constituent of many ceramic materials and natural rocks. Thermodynamic properties of this aluminosilicate depend on ordering of Al and Si cations on tetrahedral sites of its lattice. Many types of Al,Si order can be distinguished in this mineral. First of all, there exist two structurally distinct tetrahedral sites T_1 and [illegible] whose average occupancies remain different (T_1 is enrich[illegible] in the high-temperature hexagonal phase. Below 1450 °C the hexagonal phase transforms into the orthorhombic phase and T_1 and T_2 site occupancies further split due to long-range ordering (LRO). ^{29}Si NMR data suggest that there also exists strong short-range ordering (SRO). The degree of SRO is very high within T_2-T_2 bonds and is relatively low within T_2-T_1 bonds.

Such complex ordering behavior is related to the complex topology of the Al,Si framework, which can be described as a sequence of layers composed of 6-member ($6T_2$) and 9-member ($6T_2 3T_1$) rings. The presence of the rings with an odd number of sites causes the „frustration effect", which leads to an effective decrease of the degree of SRO within T_2-T_1 bonds. The preference of Al for the T_1 sites is caused by a closer proximity of these sites to the Mg-sites.

Our cluster variation model is based on 18-point and 15-point clusters and is designed to describe all these complex ordering phenomena. Preliminary testing of the model has shown its ability to quantitatively describe ^{29}Si NMR spectra of synthetic Mg-cordierites with variable degrees of SRO and LRO and to extract reasonable values of the configurational Al,Si entropy from the spectroscopic information.

B26

Coupled thermodynamic and kinetic models for high temperature processes

Pertti Koukkari and Karri Penttilä

VTT Chemical Technology, P.O. Box 1404, FIN 02044-VTT, Finland

Thermochemical simulation of reactive high temperature mixtures has been performed by combining overall reaction kinetics with the multi-component Gibbs energy minimisation. Thus, the the mass and heat transfer conditions of the reactor can be combined with the enthalpy changes due to chemical reactions and, consequently, the change of temperature in the reactive system can be evaluated in terms of the extent of the overall reaction. The calculation method thence allows for the effect of the changing temperature on the reaction rates to be taken into account during the course of sequential process simulation.

As a result of the multi-component simulation, a series of time-dependent intermediate thermochemical states is received. For each intermediate state, both intensive and extensive state properties become calculated, among them the molar amounts of the multi-component species. The chemical species present in each intermediate state are virtually independent and there is a chemical potential assigned to each of these species. The gradual chemical change in the thermodynamic system proceeds from the initial state of mixed reactants to the final state of product mixture. Both stationary and transient phenomena may be calculated.

The method has been applied e.g. to a high temperature Titanium(IV)Chloride burner and to a rotary drum with chemical reactions. A fair agreement between the calculated and measured data has been obtained.

The coupled thermodynamic and kinetic models can be constructed with well-known Gibbs energy minimiser routines such as Solgasmix and ChemApp. A practical approach is that of ChemSheet, which operates the ChemApp thermochemical library in a multi-disciplinary way from Excel-spreadsheets. Examples of coupled thermodynamic and kinetic models operable in ChemSheet will be given.

Thermodynamic modelling of oxide solid solutions and melt processing of Bi-2212 superconductors

Bengt Hallstedt and Ludwig J. Gauckler,
ETH Zurich, Department of Materials, Institute of Nonmetallic Materials, Swiss
Federal Institute of Technology, CH-8092 Zurich, Switzerland

$Bi_2Sr_2CaCu_2O_z$ (Bi-2212) and $Bi_2Sr_2Ca_2Cu_3O_z$ (Bi-2223) are two of the most promising compounds of the ceramic superconductors for bulk applications. In order to produce dense single phase material it has turned out to be necessary to partially melt the material during processing. The resulting microstructure and superconducting properties are sensitively dependent on the processing conditions. Due to the complex phase relations around these phases very large efforts have been necessary to understand the basic reaction sequences during melt processing and, thus, to be able to control the final properties. As a substrate during processing Ag is usually used. Ag dissolves in the liquid phase but not in the solid phases. Thermodynamic modelling offers valuable help in understanding the reaction sequences during melt processing and the influence of various processing conditions on the resulting microstructure. We have modelled the Ag–Bi–Sr–Ca–Cu–O system using Calphad technique.

In the present work we will concentrate on three topics:

- We will discuss thermodynamic modelling of oxide solid solution phases using the compound energy formalism. This will be illustrated by the modelling of the spinel phase in the MgO–Al_2O_3 system and the $Bi_2Sr_2CaCu_2O_{8+\delta}$ phase.
- Several subsystems of the Ag–Bi–Sr–Ca–Cu–O system were experimentally completely unknown. We will use the Ag–Bi–O system as an example to show how the CALPHAD technique can be combined with experimental work to efficiently treat unknown systems.
- Using thermodynamic calculation and comparisons with experimental work we will discuss melt processing of Bi-2212 on Ag substrates.

B28

KINETIC MODELLING OF SYNTHESIS OF TITANIUM CARBIDE

Guangqing Zhang and O. Ostrovski
School of Materials Science and Engineering, University of New South Wales,
Sydney 2052, Australia
E-mail: G.Zhang@unsw.edu.au; O.Ostrovski@unsw.edu.au

In the kinetic modelling, titania reduction by methane-hydrogen-argon gas mixture to titanium oxycarbide, is represented by two reactions:

$$TiO_2 + (H_2 + CH_4) \rightarrow \tfrac{1}{2}Ti_2O_3 + H_2O + CO$$

$$\tfrac{1}{2}Ti_2O_3 + (\tfrac{1}{2} + x)CH_4 \rightarrow x(TiC)_{\text{solid solution}} + (1 - x)(TiO)_{\text{solid solution}} + (\tfrac{1}{2} + x)CO + (1 + 2x)H_2$$

Under experimental conditions, the rates of both reactions were controlled by intrinsic kinetics. A two-interface shrinking unreacted core model and a crackling core model are employed for the kinetic modelling of reduction and carburisation reactions. The extent of the total reduction as a function of reaction time is described analytically. Two models give close results, which are consistent with experimental data obtained at 1473 - 1723 K and methane content less than 8 vol.%.

Taking into Account Systematic Errors During Simultaneous Assessment of Materials Properties

E.B. Rudnyi

Chemistry Department, Moscow State University, 119899 Moscow, Russia
rudnyi@comp.chem.msu.su, http://www.chem.msu.su/~rudnyi/

The advances of material science depends heavily on reliable thermodynamic databases which allow us to optimize the synthesis conditions for the given material and to predict its behavior in different media. In order to compile the database required, the raw experimental values obtained in heterogeneous experiments (the heat capacities, the enthalpies, the values for phase equilibria, etc.) are to be processed simultaneously. One of the problems is tied with systematic errors, when the differences between results of different authors are greater than the data scatter within a single experiment. In our view, the application of modern methods devised in mathematical statistics [1] allows us to treat this problem, at least partly.

In order to describe the systematic errors the two new terms are added to the error model

$$y_{ij} = f_i(x_{ij}, z_i; \Theta) + \varepsilon_{r,ij} + \varepsilon_{a,i} + \varepsilon_{b,i}(x_{ij} - x_i) \qquad (1)$$

where it is assumed that there are results of M experimental series and each series comprises N_i experimental points - $\{y_{ij}, x_{ij}, z_i\}$; $i = 1, ..., M$; $j = 1, ..., N_i$. x_{ij} is the input, y_{ij} is the output, z_i is the vector of constant values for the i-th experiment, notation f_i says that the theoretical model may be different for different series, $\varepsilon_{r,ij}$ is the reproducibility error (experimental noise). The total systematic error (laboratory effect) is suggested to compose of a shift error ($\varepsilon_{a,i}$) and a tilt error ($\varepsilon_{b,i}$). The vector of unknown parameters Θ and unknown error variances can be determined simultaneously by maximizing the likelihood function.

Several case studies for the application of the model (1) are presented. This includes the equilibria with high-temperature superconductors $YBa_2Cu_3O_{6+z}$, $YBa_2Cu_4O_8$, $Y_2Ba_4Cu_7O_{14+w}$, thermodynamic properties of calcium aluminates, and the binary phase diagrams of Ba-Cu, Cu-Y, Hg-Te, and Bi-Se.

The special attention is paid to the comparison of the results obtained under the model (1) with those of the conventional weighted least squares. Note that the latter is the special case of the model (1) when all the systematic errors, $\varepsilon_{a,i}$ and $\varepsilon_{b,i}$, are assumed to be zero. The questions of the visualization of the fit and the role of the expert are also discussed.

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B 30

"The problem of properties modeling in associated solutions."

Prof. Maksymilian Sukiennik, dr. Krzysztof Gargul
Mining and Metallurgy University
Faculty of Non-Ferrous Metals,
Al. Mickiewicza 30,
30-059 Kraków
Poland

The problem of thermodynamic properties modeling in liquid metal solutions with intermetallic compounds was analysed in this paper. Wide known literature models (IAS, Jordan's, Algers's, etc.) give various results for the same alloy.

Therefore the authors made the detailed analysis mentioned literature models. The issue of this work is the conclusion that the functions of logarithm activity coefficient ($\ln\gamma_1$, $\ln\gamma_2$) taken into account during calculations especially influence on results obtained from model propositions.

Enhanced Volatilization of Uranium Dioxide in Presence of Water Vapor

L.N. Gorokhov and I.V. Sidorova
Glushko Thermocenter of RAS, 13/19 Izhorskaya st., 127412 Moscow, RUSSIA

The interaction of uranium dioxide with water vapor at high temperatures results in oxidation and significant enhancement of volatility. This enhancement is usually ascribed to the formation of $UO_2(OH)_2$ molecules. However, some other UO_xH_y molecules can play an important role in the enhancement of UO_2 vaporization as well. To clarify the situation, thermodynamic calculations for the $UO_2(s) - H_2O(g)$ system were carried out taking into account UOH, UOOH, $UO_2(OH)$, and $UO_2(OH)_2$ molecules. Thermodynamic functions for UO_xH_y molecules were calculated using molecular parameters and enthalpies of formation estimated by comparison with UO_xF_y molecules. The results demonstrate dramatic increase of uranium dioxide volatility in presence of water vapor at $p = 1$ bar, due to formation of UO_3, UO_2OH and $UO_2(OH)_2$ molecules.

This work was supported by the Russian Federation for Basic Research (RFBR Project 94-03-09749).

B32

A THERMODYNAMIC MODEL OF AMORPHOUS GRAIN BOUNDARY PHASE IN LIQUID-PHASE SINTERED β-SiAlON CERAMIC

J.A. Golczewski, H.J. Seifert and F. Aldinger

Max-Planck-Institut für Metallforschung and
Institut für Nichtmetallische Anorganische Materialien, Universität Stuttgart
Pulvermetallurgisches Laboratorium, Heisenbergstr. 5
D-70659 Stuttgart, Germany

Thermodynamic modeling has been developed to explain the apparent stability of intergranular amorphous phases in liquid-phase sintered ceramics. The basic postulate has been to consider such grain boundary phases as separate phases of the system. An analytic form of the Gibbs energy functions recently derived for amorphous silicates has been taken to describe this boundary phase. An equilibrium condition conforming with construction of parallel tangents of Gibbs energy functions considered has been used to derive the compositions of the bulk and the boundary phase. Microstructure of liquid-phase sintered β-SiAlON ceramic has been ascertained in this way. This model approves existence of amorphous boundary phases as thermodynamically stable and determines a relation between their amount and composition of sinter additives in agreement with experimental evidences.

The computer realization of U - algorithm of thermodynamic calculation of isothermal sections of phase diagrams of ternary systems. Application to the Ni-Al-W system.

A.L.Udovsky[1),2)], M.V.Kupavtsev[2)]
[1)]-Baikov Institute of metallurgy and Materials Science of RAS
Leninsky Prospecr,49, Moscow,117334, Russia;E-mail udovsky@ultra.imet.ac.ru
[2)]- Moscow Engineer -Physical Technical University
Kashirskoe shosse, 31, 115409, Moscow, Russia

For receiption of optimized description as phase diagram (PD), as thermodynamic properties (TP) of alloys of ternary systems(3CS) was necessary to be decided indirect thermodynamic task. The opportunity of decision of the lat-ter is considerabl limited by absence of autonomic computer programs (ACP) for calculations of PD and TP of alloys, including multiphase conditions. Under ACP for as PD, as TP the use as input data any significances of stability parameters (SP) and interaction parameters (IP) for all considered phases in given interval of temperatures without tasks initial values for searches as two-phase tie-line, as three-phase tie-plane of calculated phase diagram is meant.

Earlier one of authors of present report has proposed as alternative of method of Newton (or Newton-Raphson method)for solving of system of equations of equilibria for two phases, which requires the task of initial approximation, the original algorithm of calculation (as U-algorithm) of PD of binary systems was offerred. The U-algorithm is generalization of Maxwell method ("equality of areas for P-V coordinates for phase transformation gas->liquid of pure substan-ces"), include the equality of areas in coordinates $\partial G/\partial x$ - x, where G-molar Gibbs energy, x-molar fraction of 2-nd component for closed binary systems.

In present work this algorithm is generalized on case of search tie-line for PD of 3CS. The computer program, realizing the U-algorithm of calculation of tie-line between two phases in ternary system is developed. The program has been tested by calculation of isotermal section at 1873 of PD of the Mo-W-Os system with use of model of regular solutions on values of PS and PI according to [1]. The example of application of developed computer program to calculation of two-phase field between melt and FCC-solid solutions in the Ni-Al-W system into in-terval 1685-1806K is discussed. Isothermal sections of liqiudus and solidus sur-faces for Ni-base FCC-solid solutions of the Ni-Al-W system is calculated

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B34

SQUARE-WELL FLUID AS A REFERENCE SYSTEM IN VARIATIONAL METHOD

Dubinin N. E., Filippov V. V.* and Vatolin N. A.

Institute of Metallurgy of the Ural's Division of Russian Academy of Sciences,
Amundsen St. 101, 620016, Ekaterinburg, Russia
*Department of Physics, Ekaterinburg Artillery Institute, 145, Shcherbakova Street, Ekaterinburg, 620108, Russia

The variational method based on the Gibbs-Bogolyubov inequality in conjunction with the pseudopotential theory had been successfully used for the investigation of liquid metal alloys thermodynamics. Earlier the hard-sphere (HS), the charged HS, the one-component plasma and the HS Yukawa models had been used as reference systems [1-3]. In the present work we used the square-well (SW) potential as a reference potential for the calculation of thermodynamic properties of liquid metal alloys. In this case the upper bound of the free energy, F, can be expressed as

$$F = F_{SW} + 2\pi\rho\int_0^\infty g_{SW}(r)\varphi(r)r^2 dr - U_{SW},$$

where ρ is atomic density; g(r) is the pair distribution function; $\varphi(r)$ is the pair interatomic potential; U is the potential energy. $\varphi(r)$ is estimated here in the framework of local pseudopotential theory using the model Animalu-Heine potential and Vashishta-Singwi exchange-correlation function. For analytical description of the SW fluid structure and thermodynamics we assume the identity of its structure to that of the HS fluid at $r<\sigma$ (σ - HS diameter) and apply the mean spherical approximation to SW potential at $r>\sigma$. Suggested approach is used for the calculation of the thermodynamic properties of pure liquid metals and expanded on binary metal mixtures.

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The work was supported by the Russian Foundation of Fundamental Research (Grant N 99-03-32317a).

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INVESTIGATION OF THE BINARY LIQUID METAL ALLOYS THERMODYNAMICS USING ORPA AND THEORETICAL DEPENDENCE OF PSEUDOPOTENTIAL PARAMETER FROM ALLOY COMPOSITION

T.V. Trefilova, N.E. Dubinin

Institute of Metallurgy of the Ural's Division of Russian Academy of Sciences,
Amundsen St. 101, 620016, Ekaterinburg, Russia

Animalu-Heine (AH) potential is one of the best and widely used local model potentials (MP). Recently [1] we suggested the following expression for the theoretical determination of the value of the AH parameter A_i for the i-th component of alloy from the value of this parameter for the same component in pure metal A_{i0} which is used as input data:

$$A_i=A_{i0}+(E_F-E^0_{F_i})(dA_i(E)/(dE)) \qquad (1)$$

where A - well depth; E_F, $E^0_{F_i}$ - Fermi energy of alloy and pure metal respectively; $(dA_i(E)/(dE)$ is the constant for the i-th component. Then we used dependency (1) in variational method for thermodynamic properties calculations of the alkali-alkali liquid alloys at different compositions [1].

In this work we combined expression (1) with the optimised random phase approximation (ORPA) for the same purposes. The ORPA is more precise method of thermodynamic perturbation theory since it allows to take the long-range oscillatory interatomic forces into consideration [2]. Obtained results are in better agreement with experiment than the ones of [1].

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The work was supported by the Russian Foundation of Fundamental Research (Grant N 99-03-32317a).

B36

NUMERICAL MODELING OF THE POSSIBILITY OF GASLESS DETONATION IN THE SYSTEM CuO+B UNDER SHOCK-WAVE LOADING IN THREE DIMENSIONAL STATEMENT

Goreiski V.A., Kim V.V.

Tomsk State University, Physics-Technical Faculty,
36 Lenin prosp., Tomsk, 634050, Russia
e-mail: vadim_kim@mail.ru

This paper is concerned with the problem of the possibility of the detonation regime in the systems capable of gasless burning under the shock-wave loading in the three dimensional statement, taking, as a case in point, CuO+B system. A three-dimensional problem of oblique high-velocity interaction of a steel capsule, containing stoichiometric porous mixture of boron and oxide of copper, with a rigid wall is considered. The diameter of the capsule is 0.00762 m, the height - 0.026 m. A model of damageable medium is used in the calculations takes into account the possibility of pores compaction or growth as well as chemical reaction. The angle of impact is 15 degrees, the impact velocity is varied in the range of 500-1200 m/s. The value of the initial porosity of the mixture was 0 and 50%. The set of equations describing time-dependent adiabatic motion of a compressible chemically active medium consist of equation of continuity, motion, energy, chemical kinetics and the equation that describes the variation the specific volume of pores. The finite-element method is used for solving the problem.

An analysis of compaction process with simultaneous chemical reaction in the powder mixture was done. Configurations of the capsule at the different stages of the process are presented. The time-dependencies for the specific volume of pores, the pressure, the temperature, the interaction force and the rate of chemical reaction are analyzed. The influence of the initial porosity and velocity of impact on the character of the process of chemical reaction in the mixture is revealed.

The research was supported by the Russian Foundation for Basic Research (Grant No. 99-03-32200).

Generalization of Chemical Potential Diagrams and its Application to High Temperature Materials Chemistry

Harumi Yokokawa, Natusko Sakai, Teruhisa Horita, Katsuhiko Yamaji

National Institute for Materials and Chemical Research, Higashi 1 – 1, Tsukuba,
Ibaraki 305-8565, Japan

Generalization of chemical potential diagrams has been made to construct those proper diagrams which should be appropriate for the application in high temperature materials chemistry. Emphasis will be placed on the inclusion of the temperature axis or the pressure axis in the chemical potential diagrams and also on disection methods to decrease the dimensionality in multicomponent systems.

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THERMOCHEMISTRY OF NON-STOICHIOMETRIC TITANIUM SELENIDES AND TELLURIDES

O.Y. Pankratova, R.A. Zvinchuk and A.V. Suvorov

Department of Chemistry, St. Petersburg State University,
St. Petersburg, Petergof, 198904, Russia

Quantitative changes of the nonstoichiometric compounds formation enthalpy within homogeneity ranges or in the such compounds series allow to estimate the bonds energies for different valency states of the atoms and relative stability of these compounds. In the systems titanium-chalcogen the broad homogeneity ranges are observed. In the interval Ti_2Ch_3-$TiCh_2$ the selenides and tellurides structures "approaches" to the CdI_2 type [1,2].

In the literature we have found the thermochemical data only for the separate stoichiometric ratios. Only for dichalcogenides the calorimetric measurements were fulfiled using the burning technique. In other cases the enthalpies of formation were received by Knudsen method or by half-empirical calculation. All these data are roughly estimated; the errors being from 10 up to 25%.

In this work the formation enthalpies $\Delta_f H^0$ were determined and enthalpy-composition relation are established in the following ranges. For $TiSe_x$: $1.45 \le x \le 1.71$ (Ti_2Se_3- Ti_5Se_8); $1.71 \le x \le 1.85$ (Ti_3Se_5). For $TiTe_x$: $1.45 \le x \le 1.65$ (Ti_2Te_3-Ti_5Te_8) and $1.95 \le x \le 2.00$ ($TiTe_2$).

We have measured the standard formation enthalpies per mole $TiCh_x$ in the thermoconducting high-temperature calorimeter with the isothermic jacket [3] in which the heat of direct synthesis of $TiCh_x$ was discharged. Tests with selenides were carried out at 880 and 550^{0}C and with tellurides at 880^{0}C. The correspondence between the calorimetric products and the thermic synthesis products was verified. Both for selenides, and for tellurides the linear character of the formation enthalpies (in kJ/mole) dependence from index (x) is found.

For selenides: $-\Delta_f H^0 = 156x + 64 \qquad \rho = 0{,}998$,
for tellurides : $-\Delta_f H^0 = 97x + 29 \qquad \rho = 0{,}980$,
where ρ - correlation factor.

The linearity of these dependencies is caused by the fact that the basic contribution in the formation enthalpies is brought by the near neighbors interaction when the ratio of different valent forms Ti (II) and Ti (IV) atoms changes monotonically [1,2].

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CALORIMETRIC STUDY OF LIQUID ALLOYS AND PATHWAYS OF REACTIONS IN THE SYSTEM Bi - Sb - Se

R. Blachnik and E. Klose

Institut für Chemie, Universität Osnabrück, Barbarastr. 7, D-49069 Osnabrück

High temperature calorimetry has been used to measure enthalpies of mixing of Bi-Sb-Se melts for five sections at 873 K and for one section at several temperatures. The experiments were carried out under dry argon using an isoperibolic heat flow calorimeter. The exothermic enthalpies decrease with higher temperatures. The enthalpy surface in the ternary system is determined by a valley of exothermic minima stretching from Bi_2Se_3 to Sb_2Se_3. The excess enthalpies were adapted with the aid of the association model [82Som] and additional interaction parameters using the least squares method [77Luk].

Mechanical treatment has been used to synthesize compounds on the Bi_2Se_3-Sb_2Se_3 section. Products of these experiments were examined with X-ray and thermoanalytical methods.

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B 40

Manometric method in scanning the phase diagrams of low volatile Gallium chalcogeniges using the auxiliary compounds

Zlomanov V.P*., Zavrazhnov A.Yu**., Turchen D.N.**., Goncharov Eu.G**.

*- Moscow State University, Moscow, Dep.of Inorg. Chemisry ** - Voronezh State University,

It is known, that the vapour pressure methods are widely applied in examinations of the phase diagrams. However, low fugitiveness of objects under exploration frequently makes it impossible to use these methods. In approximation of a neiglibly small solubility of the third, auxiliary component in condensed phases of the binary system 2 new ways permitting to apply a zero - manometric method for scanning of the phase diagrams and homogeneity regions of low-volatile binary compounds have been designed. In the first of these ways the third component *is put into the chemical interaction with substances being explored.* The choice of this auxiliary component is carried out so that the interaction is accompanied by the selective transfer into a vapour of one of the component of explored binary system (in the form of its fugitive compound(s) with the third component).

It has been shown, that with the help or the offered way the construction of the phase diagrams of the definite binary compounds (GaSe, GaS) is possible. In the role of the auxiliary component iodine and chlorine are used (in the starting form as $GaHal_3$). These components form the fugitive compounds, bonded by the following equilibrium:

$$2/x\ Ga_nCh + GaHal_{3\,(gas)} = 2/x\ Ga_{n-x}Ch + 3\ GaHal_{(gas)} \quad \Delta H > 0\ (1).$$

In eq. (1) Hal means Cl or I and Ch is S or Se. The formulas Ga_nCh and $Ga_{n-x}Ch$ depending on the character of equilibrium mean or 2 different phases, or 1 phase of variable composition.

In second of the applied ways the borders of the of homogeneity regions of the phases are scanned at temperatures above eutectic (monotectic) one. For this purpose the indifferent gas (Ar, GaI), sparingly soluble in a melt is inlet into the contact with the equilibrium mixture of the explored solid phase and the melt; then the temperature dependence of the gas pressure in the three-phase equilibrium “S-L-V” is being studied. The definition of a solidus line becomes possible using the of the rule of lever and Henry law.

With the help of the first way it is established, that at the temperature range up to ~ 1100 K the phases of GaSe and GaS are placed in the field of a gallium excess. Under that conditions the GaSe homogeneity region has the width of 0.10 - 0.15 at. %, and the selenium border of this region and the stoichiometry composition close together. With the help of both ways it is shown, that at the temperatures of GaSe premelting the anomalously sharp expansion of the homogeneity region of this phase to the side of selenium is occured (up to the composition of 50.60 at. % Se). Contrary to GaSe, the phase of GaS is characterized by the relatively narrow homogeneity region (< 0.08 at. of %) without the sharp expansion near the GaS melting point.

PARTITION OF ALLOYING ELEMENTS BETWEEN γ(A1) AND δ(Ni_3Nb:D0a) PHASES IN THE Ni-Fe-Cr-Nb BASE SYSTEMS

R.Kainuma, Y.Inohana, I.Ohnuma and K.Ishida

Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-ku, Aoba-yama 02, Sendai 980-8579, Japan.

Recently, the present authors' group has investigated the partition behaviors between some intermetallic phases in the Ni-Al base superalloys.(1,2) The Ni_3Nb intermetallic compounds such as metastable γ"($D0_{22}$) and stable δ(D0a) phases, appear in the Ni-Fe-Cr-Nb (Inconel 718) base system which play an important role in the high temperature Ni base superalloys. In the present study, partition of alloying elements (Al, Si, Ti, V, Mn, Co, Cu, Zr, Mo and W) between γ(A1) and δ in the Ni-Fe-Cr-Nb base systems is studied mainly using the diffusion couple method. The data regarding the effect of alloying elements on the relative stability of those phases will be useful for the alloy design in Ni-Fe-Cr-Nb base superalloys.

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GIBBS ENERGY AND ENTHALPY OF FORMATION FOR TERNARY ALKALI METAL ALLOYS AT TEMPERATURES UP TO 1200K

D.N. Kagan, G.A. Krechetova, E.E. Shpilrain

Institute for High Temperatures of the Russian Academy of Sciences (IVTAN)
IVTAN, Izhorskaya 13/19, Moscow 127412 Russia

Results of thermodynamic properties investigation of a ternary system Na-K-Cs in the entire area of concentration triangle in the temperature interval from 200 to 1200K are presented. The method of research is based on experimental determination of partial enthalpy of formation $\Delta \overline{H}_i$ for liquid-metal alloy in all temperature range under study and thermodynamic activity a_i of liquid components at only one reference temperature $Ti = 400K$. The experimental data obtained are input values for solution of chemical thermodynamics differential equation $[\partial \ln a_i / \partial(1/T)]_{p,xi} = \Delta \overline{H}_i / R$, being, respectively, integrable function $\Delta \overline{H}_i = f(T, x_i)$ and boundary condition $a_i = \xi(T_i, x_i)$. Thus, the method allows to determine partial Gibbs energy $\Delta \overline{G}_i = RT \ln a_i$ in the high temperature area without resorting to its direct measurements in this area which would be extremely difficult with respect to alkali metals. Detailed algorithm of the method, instrumentation and results for alkali metal binary systems were discussed at HTMC-VIII; features of azeotropic systems with continuous series of solid solutions are analyzed in our contribution to HTMC-IX. This paper develops the method for ternary systems.

Despite that the method suggested significantly reduces required scope of measurements, it remains rather extensive since functions $f(T, x_i)$ and $\xi(T_i, x_i)$ are to be determined in the entire concentration triangle area. Therefore, considering experimental data for all three boundary binary systems obtained earlier, it was thought expedient to use the above general method only for some test composition of investigated ternary system, and then use an adequate model theory as an interpolation tool providing terminal passage to an appropriate binary system at $x_{i(j,k)} = 0$ and to experimentally investigated above ternary system composition at $x_{i,j,k} = x_{i,j,k}^{exp}$. An eutectic alloy composed (in atomic fractions) of 0.139Na-0.435K-0.426Cs was selected as a ternary test composition. Data for this composition serve not only to the indicated purpose but are important as such, since this eutectic alloy represents technically important system with the minimum crystallization temperature among all metal fluids known on the Earth, ($T_{cryst.} = 195K$), being both highly effective high-temperature and low-temperature coolant for technological and power units. Model theory selection was based on calculation of configuration energy change when forming the ternary alloy in quasi-chemical approximation.

The results reveal inversion of excessive partial Gibbs energy $\Delta \overline{G}_i^* = RT \ln \gamma_i$ (where γ_i is liquid component activity coefficient) with growth of temperatures for K and Cs and, respectively, change of sign for the components partial pressure deviation, as well as the total pressure, from the Raoult's one. The results obtained may be interpretation of data contained in the literature on this phenomenon observed in independent saturation pressure measurements.

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THERMODYNAMIC FUNCTIONS OF AMORPHOUS ALLOYS Co-Si-B

*V.Goryacheva**, *I.Kutsenok**, *O.Vassilieva***, *I.Tomilin***
*Moscow State University, Chemistry Department, Moscow, 119899, Russia
** Moscow Institute for Steel and Alloys (Technical University).

The determination of partial thermodynamic functions of Co ($\Delta\mu_{Co}, \Delta\overline{H}_{Co}, \Delta\overline{S}_{Co}$) in amorphous alloys Co-Si-B was conducted by emf-method in electrochemical cells:

$$- \text{Co} \mid \text{KCl+CoCl}_2\text{+glycerin} \mid \text{Co-Si-B} +$$

at 370-450K [1]. Four samples of this system $Co_{0.68}Si_{0.107}B_{0.21.3}$, $Co_{0.75}Si_{0.085}B_{0.165}$, $Co_{0.75}Si_{0.125}B_{0.125}$, $Co_{0.75}Si_{0.165}B_{0.085}$ were studied. X-ray diffraction method was used for checking amorphous state of these alloys before thermodynamic experiments.

The values of obtained partial thermodynamic functions are presented below:

Constitution of alloys	$\Delta\mu_{Co}$ at 420K, kJ/mol	$\Delta\overline{H}_{Co}$, kJ/mol	$\Delta\overline{S}_{Co}$, J/K mol
$Co_{0.68}Si_{0.107}B_{0.21.3}$	-12.89 ± 0.89	-53.8 ± 2.2	-97.4 ± 5.2
$Co_{0.75}Si_{0.085}B_{0.165}$	-11.94 ± 0.78	-49.3 ± 4.0	-89.0 ± 9.6
$Co_{0.75}Si_{0.125}B_{0.125}$	-11.04 ± 0.95	-53.5 ± 3.8	-101.1 ± 8.9
$Co_{0.75}Si_{0.165}B_{0.085}$	-12.04 ± 0.76	-55.3 ± 3.1	-103.0 ± 7.3

It could be concluded that the chemical potential of Co in the first of alloys is more negative then in other ones. This conclusion is in a good agreement with thermodynamics of solutions theory. For three alloys containing 75 at.% Co the chemical potentials of Co are approximately equal taking into account the experimental accuracy. The similar phenomenon was observed earlier in our previous paper [2].

Large negative values of $\Delta\overline{S}_{Co}$ could be apparently explained by existing excess terms in Gibbs energy of quenched alloys in comparison with Gibbs energy of thermodynamically stable samples.

This study was supported by the Russian Foundation for Basic Research (award number 97-03-333630A)

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An experimental study on thermodynamics of Cu-As liquid solutions

B. Onderka[1], T. Pomianek[2], J. Romanowska,[2] G. Wnuk[2] and J. Wypartowicz[1]

[1]Institute of Metalurgy and Materials Science Polish Academy of Science, Reymonta St. 25, 30-059 Kraków

[2]Rzeszów University of Technology, W. Pola St. 2, 35-959 Rzeszów

The thermodynamic description of liquid phase in copper-arsenic system is still insufficient, despite several experimental studies. Taking into account numerous applications of these data in considerations of multicomponent systems of practical importance in metallurgy (with sulpur, iron, nickel, arsenic etc.) further progress in this topic is needed. The activity coefficient of arsenic in Cu-As at 1175-1473 K insreases strongly (5 orders of magnitude) in the composition range between dilute solution and the equimolar one, which causes serious experimental difficulties. This study presents results of assesment for liquid phase based on experimental data, including our recent work carried out by means of equilibrium vapour saturation technique. The liquid Cu-As alloy was dynamically equilibrated in semi closed graphite cell with the reference Sn-As liquid alloy through gaseous phase, containing arsenic and argon. The thermodynamic description of reference liquid Sn-As alloy had been evaluated from experimental data, including our isopiestic experiments. The method provides good control of temperature and equilibrium alloy composition. The experiments covered the temperature range 1173-1373 K. Liquid phases in Sn-As and Cu-As systems were optimised as substitutional solutions.

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Prediction of Thermodynamic Properties and Stability for Solid Chemical Compounds

G.F.Voronin

Chemical Department, Moscow State University, 119899 Moscow, Russia

The possibility of prognostication the thermodynamic properties and stability for a series of compounds comprising the same components from the known properties of some of these series members is considered. The question is about the "weak" phases with low stability in reference to the other "strong" phases of the same system. Such partition of the phases on two ranks can be done usually on the base of (T-x)-phase diagram without knowledge of their thermodynamic properties. A model for description the composition dependence of the thermodynamic properties of low-stable compounds by unitary analytic function is suggested. In consider heterogeneous system this function represents an envelope for a broken line or surface and resembles the known formulas for regular solutions.

Stability analysis formulated with the model under consideration makes it possible to find the most probable set of compounds stable in composition interval limited by the phases of reference. For control systems the composition of compounds and their thermodynamic properties calculated in this way correspond very well to the studied sets and properties of compounds. This approach was applied to estimating or refining the thermodynamic properties of many phases in the binary, ternary and quaternary systems from the metals, oxides, and salts.

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ON RELATIVE OXOACIDIC PROPERTIES OF THE EUTECTIC MELT $BaCl_2$-KCl-NaCl (0.43:0.29:0.28) at 700°C

V.L.Cherginets, O.V.Demirskaya and T.P.Rebrova

Institute for Single Crystals of National Academy of Sciences of Ukraine,
Lenin ave., 60, Kharkov, 310001, Ukraine

Acid-base reactions in ionic melts are essentially affected by simultaneous reactions of melt cations with oxide ions. A degree of oxide ion fixation is dependent on acidities of melt cations, and it is the constant for the melt (oxobasicity index, pI_l), allowing to estimate behaviour of Lux acids and bases in said melt. We developed the method of the oxobasicity indices estimations based on solubility data.

Acidic properties of the $BaCl_2$-KCl-NaCl (0.43:0.29:0.28) eutectic at 700°C as compared with KCl-NaCl have been studied by a potentiometric titration technique using a membrane oxygen electrode $Pt(O_2)|ZrO_2(Y_2O_3)$.

Solubility products of MgO, NiO, CoO, MnO, ZnO,CdO, and acidic properties of Ca^{2+} have been determined to be essentially higher than in KCl-NaCl eutectic. There was no CaO precipitation observed although Ca^{2+} possessed appreciable acidic properties. An average shift of *-log*K (molar fraction scale) *vs* KCl-NaCl melts, numerically corresponding to the oxobasicity index of $BaCl_2$-KCl-NaCl (0.43:0.29:0.28), was ~2.01(±0.3).

Acid-base pair	Values of –*log*K		$pI_l \equiv \Delta(-log pK)$
	KCl-NaCl	$BaCl_2$-KCl-NaCl	
Mg^{2+}/MgO	11.62±0.06	9.76±0.12	1.86
Ni^{2+}/NiO	11.38±0.06	9.26±0.11	2.12
Co^{2+}/CoO	10.24±0.03	8.12±0.12	2.12
Mn^{2+}/MnO	9.13±0.05	7.38±0.06	1.75
Zn^{2+}/ZnO	9.28±0.20	6.97±0.06	2.31
Cd^{2+}/CdO	7.54±0.03	5.43±0.13	1.92
Ca^{2+}/CaO	–	2.65±0.12	–

SOLID SOLUTIONS IN THE Y_2O_3-BaO-WO_3-CuO SYSTEM

T. N. Kol'tsova , G. D. Nipan, K. S. Gavrichev

N.S. Kurnakov Institute of General and Inorganic Chemistry,
Russian Academy of Sciences, Leninsky prosp. 31, Moscow, 117907, Russia

The new phases were detected in quaternary Y_2O_3 - BaO - WO_3 - CuO oxide system, their structures and superconducting properties were investigated. The phase diagram of quaternary oxide system was constructed.

The study of $YBa_2W_nCu_zO_{7\pm\delta}$ samples showed that dark-brown phase with $YBa_2W_{0.5}Cu_{2.5}O_x$ (or $Y_2Ba_4WCu_5O_x$) was crystallized in the cubic system (F space group) with lattice parameter $a = 8.395$ Å and had negligible amount of $YBa_2Cu_3O_{7-\delta}$ as admixtural phase. No superconducting properties were detected. The thermal studies of $Y_2Ba_4WCu_5O_x$ carried out in air allowed to find that oxygen desorbtion begins above 420°C and increases at two solid -phases transformations (endoeffects at 928 and 950^{0}C).

Comparison of our and literature data revealed that the $Y_{2/3}Ba_2WO_x$, YBa_2WO_x, $Y_{0.25}Ba_2Cu_{0.75}WO_x$, $YBa_4W_2CuO_{12}$ and $Y_3Ba_3WCu_6O_x$ were the compositions of the same solid solution with cubic structure and lattice parameter in the range: $a = 8.31 - 8.40$ Å .

The $YBa_2W_2CuO_x$ sample was identified as single-phase which actually is solid solution based on $BaWO_4$ and crystallized in tetragonal system (I - space group) with the lattice parameters: $a = 5.603$ Å and $c = 12.730$ Å.

The detail X-ray study of $YBa_{1.5}W_{0.5}Cu_3O_x$ (or $Y_2Ba_3WCu_6O_x$) sample showed that this dark-brown phase is crystallized in monoclinic system ($P_{2/m}$ -space group) with lattice parameter: $a = 11.357$Å, $b = 6.298$Å, $c = 4.999$Å and $\beta = 104.49°$ .The studies of magnetic susceptibility revealed that this phase had superconducting properties (T_c - near 90K).

The $YBaWCu_3O_x$ composition was detected as single-phase in barium-to-tungsten substituted series. The green-color $YBaWCu_3O_x$ was crystallized in orthorhombic system with lattice parameters: $a= 5.612(4)$Å, $b= 10.237(6)$ Å, $c= 12.62(3)$ Å. The orthorhombic phase had wide homogeneity range: the $YBaWCu_3O_x$, $YBaWCuO_x$, $Y_2BaWCuO_x$, $YBa_{0.7}W_{1.3}Cu_3O_x$ compositions were confined in this homogeneity range.

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The In-Pd-Sb phase diagram

H. Flandorfer, C. Luef and H. Ipser
Institut für Anorganische Chemie, Universität Wien
Währingerstraße 42; A-1090 Wien, Austria

The importance of III-V compound semiconductors for electronic and optoelectronic devices has constantly increased in recent years. Of these InSb belongs to the „narrow band-gap semiconductors“ where the excitation energy is in the range of the infrared region of the electromagnetic spectrum. Therefore these compound semiconductors are used as infrared transmitters and receivers.

An important criterion for the performance and the durability of such electronic devices is the quality of the contacts to the external current circuit. The requirements for a suitable contact material are high thermal and electrical conductivity as well as morphological uniformity and thermodynamic stability. Additionally it has to resist considerably high temperatures during manufacturing and operation. The main components of most of the currently used contact materials are Ni, Pd or Pt. To find out, which elements or alloys are stable in contact with the (III-V)-semiconductor, the ternary M-III-V phase diagrams (M = metal) provide important information.

In the present work we investigated the ternary Pd-In-Sb phase diagram up to 50 at% Pd. Apart from various information about the bordering binary systems we found an isothermal section at 500°C in the literature [71Bor]. Employing X-ray diffraction methods, DTA and metallography (including EPMA) we evaluated three isothermal sections at 300°C, 500°C (reinvestigation) and 700 °C. Furthermore some isopleths, the liquidus surface and the SCHEIL diagram were constructed.

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THERMODYNAMIC PROPERTIES AND THE PHASE DIAGRAM OF Al-RICH PART OF Al-Li-Cu SYSTEM

W.Gąsior*, Z.Moser,* B.Onderka*, F.Sommer** and B.Kim**
*Institute of Metallurgy and Materials Science, Polish Academy of Sciences , 30-059 Kraków, Reymonta Street 25, POLAND
**Max-Planck-Institut für Metallforschung ,Seestr.75, D-70174 Stuttgart,GERMANY

Emf measurements were done by means of concentration cells with molten salt electrolyte for liquid and solid Al-Li-Cu alloys at three sections with constant ratios $X_{Al}/X_{Al}+X_{Cu}$= 0.7, 0.8 and 0.9. Measurements for $X_{Al}/X_{Al}+X_{Cu}$ = 0.7 were done using two phase (Al-Li) reference electrode at constant temperatures 778 and 828 K , while for remaining two ratios 0.8 and 0.9 only at 888 K and with pure Li as a reference electrode. The resulting Li activities were combined with enthalpies of mixing of liquid alloys from calorimetric studies [93Kim] at $Al_{0.8}Li_{0.2}$ - Cu (986 K) and at $Al_{0.86}Cu_{0.14}$ - Li (945 K) and used with other previously published data for phase diagram calculations by Thermo-Calc programs. For optimizing by PARROT module in addition to described data of this study (emf and calorimetry), binary parameters from [98Ans] with various ternary phase equilibria discussed by [88Ans], [91Har] , [92Sau] and additionally completed by [91Chen1],[91Chen2] were used. Resulting temperature and compositions of the liquid invariant reactions in Al-Cu-Li system, enthalpies of formation of ternary phases T_1 , T_2 ,T_B and R, the calculated isothermal sections and liquidus surface are in reasonable agreement with results of previous calculations and compilations.

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Thermodynamic and structural characterization of the $UFeO_4$ and U_3FeO_{10} compounds.

D. Labroche, J. Rogez*, J.P. Laval**, O.Dugne
CEA-VALRHO, DCC/DTE/SIM, BP 111, 26702 Pierrelatte Cedex – FRANCE
* CTM, 26 rue du 141 ème RIA, 13003 Marseille - FRANCE
** LMCTS, URA-CNRS n°320, 123 Av. A. Thomas, 87060 Limoges - FRANCE

In order to establish the whole ternary phase diagram (U-Fe-O) which is one of the main systems in the nuclear safety program, the thermodynamic and structural studies of the $UFeO_4$ and U_3FeO_{10} compounds are performed. Even if these compounds have been already elaborated since 1964, no thermodynamic data are available and the structures are only partly known.

The experimental thermodynamic study presented here consists in the determination of the enthalpies of formation of the $UFeO_4$ and U_3FeO_{10} compounds by different solution calorimetries at two temperatures. The references are simple oxides in the binary side diagrams. The ambiant solution calorimetry is performed in aqueaous acid solvent and the high temperature one, in borate baths. The heat capacities between the two temperatures are derived from drop calorimetry measurements. This set of complementary measurements aims to give some coherent data for the further optimization.

Some structural (XRD, Neutron diffraction) and physicochemical (EDS, WDS, XRD) characterizations are achieved to determine :

- the temperature range of stability of $UFeO_4$ and U_3FeO_{10},
- the crystallographic structures,
- the nature of the structural defaults.

These informations help us in the choice of the sub-lattice selected to described the ternary phases.

Equilibrium experiments at 1300 K show how the two compounds are involved in three phases equilibria in that isothermal section of the (U-Fe-O) system.

All these measurements permit us to complete the physicochemical description of the $UFeO_4$ and U_3FeO_{10} compounds. These new data are introduced in the final optimization of the (U-Fe-O) system with the Thermocalc code.

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Enthalpies of Formation of Liquid Binary Ni + (Ti, Zr, and Hf) Alloys

M.A. Turchanin[1], I.V. Belokonenko[1], P.G. Agraval[1], and A.A. Turchanin[2]

[1]Donbass State Mechanical Engineering Academy, Kramatorsk, 343913, Ukraine
[2]Moscow State Steel and Alloys Institute, Leninky prosp. 4, Moscow, 117936, Russia

The enthalpies of formation of liquid binary Ni + (Ti, Zr, and Hf) alloys were investigated by direct solution calorimetry in the wide range of compositions at 1873K. The molar enthalpies of mixing in all systems were found to be negative with the minimum values approaching ñ41.6(1.1 kJ mol-1 at xTi = 0.37, -47.0(1.7 kJ mol-1 at xZr = 0.38, and ñ49.6(1.8 kJ mol-1 at xHf = 0.40.

The results were compared with the thermodynamic data available in literature and discussed in connection to the equilibrium phase diagrams. The temperature-concentration trend of the excess properties of mixing were simulated with an ideal association solution model. The correlation between the experimentally observed compositions of glass formation and properties of liquid alloys in investigated systems was found: amorphisation is observed in the composition ranges where a sum of the components activities calculated at the liquidus temperature is no more than 0.6-0.7.

Glass forming ability of the systems was discussed in terms of Gibb's energies of undercooled liquid phase, as well as equilibrium and non-equilibrium crystalline phases.

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Physical and Chemical Properties and Structure of Metal-Non Metal High Temperature Solutions

N. Shelkova, A. Zaitsev, B. Mogutnov
Institute for Metal Physics and Functional Materials, I.P.Bardin Central Research Institute for Ferrous Metallurgy
9/23 2-nd Baumanskaya Ul., Moscow 107005, Russia

The thermodynamic properties of a wide class of melts, which have only one feature in common, strong interparticle interaction with prevalence of covalent bonding, are perfectly approximated by the model of associate solutions. Essentially important is that the thermodynamic characteristics of the same reactions of association remain constant when the composition and the number of components change. These characteristics correlate with thermodynamic functions of formation of solid compounds close on stoichiometry and change according to a rule of an electronegativity. These allow suggestion that the parameters, describing thermodynamic behaviour of molten mixtures in wide temperature and concentration ranges, contain also information necessary for adequate approximation structure - sensitive properties particularly such as viscosity connected directly interparticle interactions and interpretation of structural data..

The purpose of this work is to demonstrate that the associated solution theory and thermodynamic characteristics explains adequately experimental data on the structure and physical and chemical properties of some liquid solutions. Firstly, the concentration dependence of isotherms of viscosity in molten manganese ñ silicon alloys was analysed. Two approaches were implemented. In one, the viscosity of the melt was considered as viscosity of an ideal mixture of associative complexes and monomer species, each being characterised by a certain viscosity. The other was based on the well-known Eyring equation, in which the excess activation energy was assumed to be equal to the Gibbs energy of formation of associates. The composition of associative complexes (MnSi and Mn2Si) and their concentrations were found according to the thermodynamic model. Good agreement with the experimental data was obtained in both cases. The results allowed us to clarify some details of the mechanism of viscous flow in the Mn-Si melt. Secondly, Bhatya-Thornton structure factors Scc(0) for Li-Pb, Na-Pb and K-Pb molten mixtures were calculated from thermodynamic data under assumption that these liquid solutions are ideal associated solutions. The results are shown to agree direct structural data.

Thermodynamics and Defect Chemistry of Mixed Oxides with Spinel Structure

Peter Franke, LTH, RWTH Aachen, Kopernikusstr. 16, D-52074 Aachen

A model for the high temperature thermodynamics and defect chemistry of ionic solid solutions with several sublattices is presented. The influence of Coulomb interactions on the internal equilibria is taken into account explicitly. A method of converting the electrostatic interactions into parameters of the compound energy model is shown. Hereby it is possible to incorporate the treatment of ionic interactions into available thermodynamic software packages without changing the code. Furthermore, in systems with several sublattices the number of parameters in the compound energy model increases dramatically with the number of species. The application of the Coulomb energy model attaches a physical interpretation to some of the parameters and the number of adjustable parameters in thermodynamic optimizations is considerably reduced.

The model is applied to fit the thermodynamic properties and defect equilibria in mixed cobalt-iron-manganese spinels, $(Co,Fe,Mn)_{3-\delta}O_4$. These materials are especially suitable for testing the thermodynamic model. Transition metal ions occur in several charge states and they can occupy different sublattices in the spinel structure. Therefore, the Coulomb energy of the crystal depends on the cation distribution. The change of the oxidation state of the ions causes a non-stoichiometric cation to anion ratio which is denoted by the symbol δ in the chemical formula. This deviation from stoichiomety is a function of the temperature, the oxygen activity, and the cationic composition. At a given temperature and cationic composition δ changes from negative to positive values with increasing oxygen activity. This behavior is related to a transition of the dominant defect type from interstitial cations at low oxygen activities to cation vacancies at high oxygen activities. In a thermodynamic optimization the parameters for the cation distribution and the defect equilibria are adjusted in order to obtain a good fit for the experimental data.

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Thermodynamic Properties of Lanthanide Triiodides in Condensed and Gaseous States

L.N. Gorokhov, G.A. Bergman, E.L. Osina, and V.S. Yungman
Glushko Thermocenter of RAS, 13/19 Izhorskaya st., 127412 Moscow, RUSSIA

Lanthanide triiodides LnI_3 have both industrial importance and fundamental scientific interest. Reliable sets of thermodynamic functions calculated using a uniform approach are necessary for treating chemical processes with participation of lanthanide iodides. The first consistent set of thermodynamic functions for all lanthanide trihalides was published by Myers and Graves (J. Chem. Eng. Data, 1977, Vol. 22, No. 4, p. 436; *ibid.*, p. 440). Since that time many new experimental and theoretical results on the properties of LnI_3 were published. For this reason, systematic analysis of new data and evaluation of molecular structure and thermodynamic properties for lanthanide triiodides has been carried out. The tables of thermodynamic functions for the following thermodynamic properties of condensed and gaseous rare-earth triiodides from La to Lu have been calculated: $C_p^\circ(T)$, $S^\circ(T)$, $\Phi^\circ(T) = -(G^\circ(T) - H^\circ(0))/T$, and $H^\circ(T) - H^\circ(0)$. The temperature range covered is from 298.15 K to 2000 K for condensed phases and to 3000 K for gases.

The main difficulty in evaluation of thermodynamic functions for solids consists in absence of low-temperature heat-capacity data for all Ln iodides except LuI_3. For this reason, lattice heat capacity of all isostructural iodides was estimated from LuI_3 data. Schottky contribution of heat capacity was estimated using literature data on Ln^{3+} ions energy levels in matrices of the same crystal symmetry. The total heat capacity values were obtained summing the lattice and Schottky contributions.

For $LnI_3(g)$ molecules, D_{3h} planar structure was accepted. Interatomic distances and vibration frequencies adopted were either based on the analysis of published data or were estimated taking into account lanthanide compression. For $Ln_2I_6(g)$ dimeric molecules D_{2h} structure was accepted. Interatomic distances and vibration frequencies were estimated. Energy levels of electronic excited states were taken into account in calculating thermodynamic functions for $LnI_3(g)$ and $Ln_2I_6(g)$ molecules.

This work was supported by the Russian Federation for Basic Research (RFBR Project 97-02-16847).

EFFECT OF TEMPERATURE ON THE SURFACE PROPERTIES OF Cu-Sn LIQUID ALLOYS

L.C.Prasad and A. Mikula
Institut für Anorganische Chemie, Universität Wien
Wahringerstraße 42 ,A-1090 , Vienna , Austria

The concentration and temperature dependence of the surface tension and surface composition of Cu-Sn liquid alloys have been theoretically investigated with the application of statistical mechanical model[1-5] based on layered structures. Our study suggests monotonic decrease in the surface tension (γ) with the increase of Sn atoms. No appreciable change in γ was observed around compound forming concentration i.e. $Cu_{0.75}Sn_{0.25}$. With regards to the effect of temperature on γ , our study shows positive temperature coefficient for all Cu - rich alloys. The temperature buffering ($d\gamma/dT = 0$)was found to occur around 30 at% Cu. It may be inferred that positive temperature coefficient might be due to progressive dissociation at the surface of atomic clusters/ associates/ complexes associated with the γ - phase of the system. So far as surface segregation is concerned, the surface is quite enriched with Sn - atoms at all bulk concentrations. However, the extent of segregation decreases with the increase of the temperature.

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Electrochemical characterization of the equilibrium between Na-β- and Na-β"-alumina as a function of the phase composition

H. Näfe*, F. Meyer, F. Aldinger
Max-Planck-Institut für Metallforschung
Pulvermetallurgisches Laboratorium
Heisenbergstraße 5, D-70569 Stuttgart,
Germany

An electrochemical approach is described which, for the first time, enables the β/β"-equilibrium in Na-(β+β")-Al_2O_3 to be characterized as a function of the phase composition. The study is based on a potentiometric solid state oxygen concentration cell. From the temperature dependence of the equilibrium constant, the thermodynamic stability of the β"-phase is determined. The results lie in the middle of a fairly large scatter range spanned by the literature data. In view of the fact that in none of the previous investigations the establishment of the β/β"-equilibrium was in-situ checked, the present findings may be regarded as much more reliable than the respective data from literature.

The present study gives evidence of the establishment of a dynamic equilibrium between the dominating phases of Na-beta-Al_2O_3 even at low temperatures, i.e. between 400 and 700 °C. This throws a light on the reliability of respective X-ray diffraction measurements which partly contradict the results of the electrochemical investigations.

High Temperature Thermodynamic Data of the Ca- and Sr- Doped $LaMnO_3$

Speranta Tanasescu, N.D.Totir, Daniela Patrascu and Doinita Neiner
Institute of Physical Chemistry "I.G. Murgulescu", Splaiul Independentei 202,
77208 Bucharest, Romania

The lanthanum alkaline earth (Ca, Sr) manganites are receiving considerable attention due to their potential application as electrode materials in solid oxide fuel cells. Besides the determination of structural and physical properties, a thorough knowledge of their thermodynamics is very important, especially as, due to the difficulties met in experimentally approaching these compounds, only few quantitative thermodynamic data are available in the literature (1-3).

As we revealed in a previous paper (3), the thermodynamic stability limits of the nonstoichiometric lanthanum and lanthanum strontium manganites are conveniently situated within the range of oxygen chemical potentials which can be measured by galvanic cells incorporating $ZrO_2(Y_2O_3)$ solid electrolyte and an iron - wüstite reference electrode.

In the present study new measurements have been made by a solid state electrochemical technique in order to characterize from the thermodynamic point of view some perovskite-type materials of general formula $La_{1-x}M_xMnO_3$ (where M = Ca; Sr and x = 0.2-0.4). The relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the partial pressures of oxygen have been obtained in the temperature range of 1073-1273 K, as a function of temperature and composition. The obtained data evidence the effect of the nature and concentration of A-site dopants on the thermodynamic properties. The results are discussed being related with the variation of the predominant defects in the oxygen sublattice.

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A Comparative Study of the Influence of Compositional Variables on the Thermodynamic Properties in the Substituted Lanthanum Manganites

Speranta Tanasescu, N.D.Totir and D.I.Marchidan
Institute of Physical Chemistry "I.G. Murgulescu", Splaiul Independentei 202,
77208 Bucharest, Romania

The study of the correlations between the thermodynamic properties and the compositional variables of the perovskite-type materials are of particular interest when the compounds are being used as electrodes in solid oxide fuel cells. In order to evaluate and optimize the properties for utilization in SOFC a better understanding of the stability limits of perovskite phases used in new cathodes materials is necessary.

The present study is a continuation of a sistematic investigation of the influence of different compositional variables on the thermodynamic data of the substituted lanthanum manganites. A solid state electrochemical technique has been employed to study the thermodynamics of the doped lanthanum manganites of general formula $La_{1-x}M_xMn_{1-y}Me_yO_3$ (where M=Ca, Sr and Me=Fe, Co) within the 1073-1273 K temperature range. The thermodynamic properties represented by the relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium partial pressures of oxygen have been obtained as a function of temperature and composition.

The influence of the oxygen stoichiometry change on the thermodynamic properties was examined using the data obtained by a coulometric titration technique coupled with EMF measurements. The results evidence new correlations existing between the thermodynamic properties, the oxygen stoichiometry change and the nature and concentration of the A- and B-sites dopants in the substituted lanthanum manganites.

Acknowledgements

The authors are indebted to the Commission of the European Communities (Science, Research and Development) for financial support in the frame of the Contract JOU 2-CT 92-0063.

We wish to thank Risø National Laboratory for supplying the solid electrolyte and Haldor Topsøe A/S for preparing the samples used in this study.

THE TI-NI-OS TERNARY SYSTEM

T.Ya. Velikanova, E.L. Semenova, T.G. Mazhuga

I.N.Frantsevich Institute for Problems of Materials Science,
Academy of Sciences of Ukraine,
3, Krzhyzhanovsky str., Kiev, 252180, Ukraine

The TiNi equiatomic compound has significant ability to transform thermoelastically. Hence the study of phase diagrams of multicomponent systems including the Ti-Ni system can be of great practical interest for the creation of new materials which demonstrate the shape memory effect. The Ti-Ni-Os ternary system is object of investigation in this work.

The Ti-Ni-Os ternary system has not been studied earlier. The confining Ti-Ni and Ti-Os binary systems were studied in [1,2]. According our data the Ni-Os binary system is a simple peritectic type.

The Ti-Ni-Os alloy phase diagram was investigated by means of metallography, powder X-ray diffraction, differential thermal and microprobe analysis in the whole concentration range and wide temperature interval up to solidus temperatures.

The ternary compounds were not found. Phases based on the Ti_2Ni, $TiNi_3$ binary compounds, the $Ti(Ni_{1-x}Os_x)$ solid solution and solid solutions on the components base take part in phase equilibria of the Ti-Ni-Os alloy phase diagram. It was established that the wide regions of the <Ni> , <Os> and <Ti> solid solutions exist in the system. The isostructural TiNi and TiOs compounds (bcc structure of CsCl type at high temperatures), melting congruently, form a continuous series of solid solutions. It allows to triangulate the Ti-Ni-Os system into two subsystems: the Ti-TiNi-TiOs and TiNi-Ni-Os-TiOs and investigate them separately.

It was shown that on the solidus surface of the Ti-TiNi-TiOs subsystem there is one $<Ti_2Ni>+<Ti>+<Ti(Ni_{1-x}Os_x)>$ three-phase region. There are two $<TiNi_3>+<Os>+<Ti(Ni_{1-x}Os_x)>$ and $<Os>+<TiNi_3>+<Ni>$ three-phase regions on the solidus surface in the TiNi-Ni-Os-TiOs subsystem.

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THE REGULARITY IN CONSTITUTION OF PHASE DIAGRAMS FOR THE TERNARY SYSTEMS FORMED BY CHROMIUM AND CARBON WITH *d*-METALS OF V GROUP

O. I. Dovbenko, A. A. Bondar and T. Ya. Velikanova

I. N. Frantsevich Institute for Problems of Materials Science
3, Krzhyzhanovsky str., Kiev, 252180, Ukraine

The alloys of indicated above systems have claimed attention for development of new materials for high temperature application.

The three systems had been investigated at not high temperatures (1050-1350 °C). The only Cr-V-C system was earlier investigated at the alloy melting temperatures, and the liquidus projection was published [1]. For the other two, the Cr-(Nb,Ta)-C phase diagrams were recently constructed at high temperatures by us.

The Cr-Ta-C and Cr-Nb-C phase diagrams are very similar by their constitutions, but they are substantially different from the Cr-V-C system. The Cr-(Nb,Ta)-C systems are analogous to the Cr-Zr-C and Cr-Hf-C systems, the Cr-V-C system – to the Cr-Mo-C and Cr-W-C systems. Phase equilibria of the Cr-(Zr,Hf,Nb,Ta)-C systems in the λ-MCr$_2$–MC$_{1-x}$–C–Cr regions are really the same. There are some differences between the temperatures of equilibria with melt participation and in homogeneity range extending (in reason of differences of atomic sizes between Cr and d-metals).

The Cr-V-C, Cr-Mo-C and Cr-W-C systems are very analogous at the subsolidus temperatures, while the high temperature phases on the base of the α-MoC$_{1-x}$ and α-WC$_{1-x}$ carbides exist. (They are isostructural to fcc d-MC carbides of the NaCl type, where d-M = Ti, Zr, Hf, V, Nb, Ta.) The great mutual solubilities between carbides of chromium and V, Mo or W are observed (in reasonable accordance, with difference of atomic sizes). There is a similarity between phase equilibria in all the regions with the exception of the VCr$_2$C$_{2-x}$ ternary phase existing field.

Thus, like the corresponding systems with d-metals of IV group the alloys of the Cr-(Nb,Ta)-C systems can be of great practical interest for development of new materials on the base of chromium-fcc carbide quasibinary eutectics [2]. They show promise as high high-temperature strength and heat resistance alloys. The complex fcc (V,Cr)C$_{1-x}$ carbides of the Cr-V-C system can be interested for using in composition materials as hard component [1].

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THERMODYNAMICAL EVALUATION OF PHASE EQUILIBRIA IN Fe-Mo-Cr SYSTEM

V.M. Danilenko, A.A. Rubashevsky, T.Av. Velikanova

I.M. Frantsevich Institute for Problems of Materials Science,
National Academy of Science of the Ukraine
3 Krzhizhanovsky Str., 252180 Kyiv, Ukraine

The Fe-Mo-Cr ternary system has not been studied in solyd state earlier. The confining binary systems, were studied [1]. In our work we obtained few expeirmental data for phase equilibria in ternary system at solydus temperature and then predicted the whole melting-crystalisation diagram by thermodynamical evaluation. For ternary solutions (BCC, σ, liquid) we have used the subregular solution model with linear temperature dependence of specific heat. The ternary compound was taken as phase with definite coustitution $Mo_{0.20}Fe_{0.57}Cr_{0.23}$.

It was found that the solid solution on base of σ-phase at the solidus temperatures has the wide gomogeneaty range and is being in aquilibria with all others of the phases system. The ternary compound melts incongruently.

Obtained model constants for all phases give possibility of thermodynamical prediction of phase equilibria in some quaternary systems such as Fe-Mo-Cr-C, Fe-Mo-Cr-Ni, Fe-Mo-Cr-Ti and other.

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THERMODYNAMIC PROPERTIES OF ALLOYS OF SCANDIUM WITH IRIDIUM

L.V.Goncharuk, V.G.Khorujaya, V.R.Sidorko

I.M.Frantsevich Institute for Problems of Materials Science,
National Academy of Science of the Ukraine
3 Krzhizhanovsky Str., 252180 Kyiv, Ukraine

Thermodynamic properties of alloys of scandium with iridium have been studied by e.m.f. measurements of concentration cells

$$(-)\ [ScSi+Si]\ |\ Sc^{+3}\ \text{ions in molten salts}\ |\ [Sc_xIr_{1-x}]\ (+)$$

in the 820-1020 K temperature range. The Sc-Ir samples whose composition corresponded to the homogeneity range of the $ScIr_3$ intermetallic compound, two-phase alloy [$ScIr_3$+$ScIr_2$] and Ir-based solid solution were investigated.

A scandium-silicon alloy from the [ScSi+Si] phase region studied previously [2] was used as the comparison electrode in order to avoid the interaction of scandium with molten salts at elevated temperatures. Vacuum-fused (10^{-2} Pa) mixtures of dried potassium, sodium and barium chlorides (melting temperature T_{melt} = 815 K) and potassium, lithium and barium chlorides (T_{melt} = 593 K) were used as electrolytes. Values of Gibbs free energy, enthalpy and entropy of formation for $ScIr_3$ (within its homogeneity range) and $ScIr_2$ phase have been determined.

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High temperature equilibria in iron rich FeVCuC alloys

R Kesri* , L Adnane* and S Hamar-Thibault**

* Laboratoire de Métallurgie Structurale, Institut de Chimie, USTHB BP 32 El Alia Alger Algérie

** Laboratoire de Thermodynamique et Physicochimie Métallurgiques, ENSEEG, BP 75, Saint Martin d'Hères, 38402 France

High temperature equilibria of quaternary iron rich FeVCuC alloys are studied by differential thermal analysis. Alloys microstructures are examined and analysed by scanning electron microscopy, electron microprobe and transmission electron microscopy.

The quaternary FeVCuC alloys with compositions lying between 5-20 wt % for V, 2-5 wt % for Cu and 1,5 - 4,5 wt % for C, are prepared from high purity materials in an arc furnace under argon atmosphere. DTA results and phases analysis permit us to relate the observed microstructures to the crystallisation paths for each alloy. The following phases are identified: primary VC_{1-x} carbides, α/VC_{1-x} and γ/VC_{1-x} eutectics, γ/C_{gr} eutectic, proeutectoid cementite, ferrite and perlite. The primary VC_{1-x} carbides are dendritic or globular, the eutectic VC_{1-x} carbides are regular, unfaceted. These carbides are sub-stoichiometric and exhibit long range order. The two ordered V8C7 (cubic) and V6C5 (hexagonal) structures has been identified. These VC_{1-x} carbides are surrounded by cementite shells. Copious precipitation of εCu appears both in the cementite surrounding the VC_{1-x} carbides, the proeutectoid cementite and the perlitic ferrite. This precipitation may occurs by interphase boundary diffusion during cooling.

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REGULARITIES OF VAPORIZATION BEHAVIOUR OF OXYACID SALTS

S.I.Lopatin

St. Petersburg State University, Chemical Department, Universitetskii pr. 2, p/o Stary Peterhof, 198904, St. Petersburg RUSSIA

The principal criterion enabling assessment of probability of competing reactions taking place is Gibbs energy value and sign. Among the most probable processes that proceed at high temperatures, the following should be listed: 1) dissociation into component oxides; 2) dissociation into free atoms; 3) evaporation without decomposition or with partial decomposition. If thermodynamical calculations for the first two processes do not cause any difficulties, calculations of reactions which involve salts of oxygen containing acids passing into vapour are more complicated due to the lack of reference data.

When considering atomization enthalpy trends in groups of gaseous salts of the type M_mXO_n (where M is a cation, X is an anion-forming element and m = 1 or 2) which form isocation series, one can see distinctly a linear dependence of $\Delta_{at}H°$salts on atomization enthalpy of gaseous anion oxides XO_{n-1}.

$$\Delta_{at}H°(M_mXO_{n-1},gas,298) = \kappa\,\Delta_{at}H°(XO_{n-1},gas,298) + b$$

Factors k and b in equation have been determined for salts of Li, Na, K, Rb, Cs, Ca, Sr, Ba and Eu. Experimental data for salts of In, Tl, Ge, Sn, Pb, B and Mg are few so far and do not allow obtaining dependencies with a high regression factor. To create a thermodynamical database, of all variety of objects of the research those should be chosen which, when evaporated, produce stable associates in the vapour. We proposed to use the value of relative radial electronegativity of salt forming oxides and their volatility as probability criteria for reactions of vapour phase synthesis, thermal dissociation or evaporation without decomposition.

Constitution of the Ternary Systems Nb-B-C and Mo-B-C

by

K.Korniyenko[1,2], A. Leithe-Jasper[3], P. Rogl[1], M. Bohn[4], E. Seidl[5]
T. Tanaka[3] and T. Velikanova[2]

[1]*Institut für Physikalische Chemie der Universität Wien, Währingerstraße 42, A-1090,Austria*
[2]*Institute of Problems of Materials Science, Ul. Krzhyzhanovsky 3, Kiev, Ukraine*
[3]*National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki, 305-0044, Japan*
[4]*UMR CNRS 6538, Centre de la Microsonde Electronique de l'Ouest. IFREMER,*
F-29263 Plouzané, France
[5]*Atominstitut der Österreichischen Universitäten, A-1020 Wien, Schüttelstrasse 115, Austria*

Abstract

The liquidus surfaces of the two ternary systems Nb-B-C and Mo-B-C have been determined by micro-optical pyrometry on sintered specimens employing the Pirani-Alterthum technique assisted by X-ray powder diffraction, light optical microscopy and EMPA. Whereas no compound formation is encountered in the Nb-system, the formation of a congruently melting ternary compound Mo_2BC (Mp=2330±20°C) characterises the liquidus projection in the Mo-B-C system. Solidification behaviour for both systems is analysed in terms of Scheil diagrams. For measurement of the eutectic temperatures in the system Mo-B-C several Pirani-samples were made. Dense sintered specimens could be achieved via isostatic pressing followed by high temperature reaction sintering under argon.

Attempts to grow large single crystals of Mo_2BC gave strong evidence for a C-deficiency in Mo_2BC_{1-x} which resulted in the formation of parasitic Mo_2C. This phase precipitates during the growth and can be found isotropically distributed within the individual grains of the crystal. Also a very pronounced trend for facetting during growth was observed. The formation of a spiral like pattern on the cut surface can be understood as an indication of significant composition fluctuations during the crystal growth.

Acknowledgements: This research was supported by the Austrian FWF under grants S5604/S5605.

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Critical review on limiting partial enthalpies of elements in liquid tin

Abeer YASSIN (*) and Robert CASTANET (**)

(*) Dept. of Physics, Univ. Baghdad, Alm-Jadriyah, Iraq
(**) Centre de Thermodynamique et de Microcalorimètrie du CNRS, 26 rue du 141eme
R.I.A., 13003, Marseille, France

Abstract

The most used and accurate method to measure the enthalpies of formation of intermetallic compounds in the solid state at room temperature is undoubtedly the dissolution method. Such a method needs the knowledge of the enthalpy of dissolution of the compound at infinite dilution as well as those of their pure components into the same solvent. The most commonly solvent used for that is tin. Tin melts at relatively low temperature (505K), it easily dissolves the greatest number of pure metals and the enthalpies of dissolution are generally small enough to minimise the errors on the determination of the enthalpy of formation of the compounds. To our knowledge, there is one general compilation devoted to the limiting partial enthalpies of metals in liquid tin which was published by Boom [1] in 1973. Since many experimental works were performed from this time, we were engaged with updating this work.

In the framework of a general compilation devoted to the enthalpies of dissolution of elements in liquid tin, the data concerning their partial enthalpies at infinite dilution in tin have been collected from literature. They were fitted against temperature and the corresponding equations are given in the paper.

Phase Equilibrium in the Al-rich Part of the Al-Pd-Co Alloy System

M. Yurechko, B. Grushko and V. Shemet*

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

** Institut für Werkstoffe und Verfahren der Energietechnik, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

The ternary Al-Pd-Co phase diagram was studied in the range of 50-100 at.% Al by optical, scanning and transmission electron microscopy, powder X-ray diffraction and differential thermal analysis. The results are discussed with the respect to the Al-Ni-Co phase diagram, which exhibits the stable decagonal quasicrystals.

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Thermal Properties of Rare - Earth Manganites with Colossal Magnetoresistance.

A.F. Maiorova, S.N. Mudretsova, A.R Kaul, O.Yu.Gorbenko, A.A.Bosak
Moscow State University, Department of Chemistry, 119899 Moscow, Russia

Colossal magnetoresistance occurs in manganite perovskites of general formula $R_{1-\delta} A_{\delta} MnO_3$ (R=rare earth elements and their mixture; A=divalent ion). The manganites exhibit a broad range of electronic and magnetic phases, covering from low-resistance ferromagnetic metals to high- resistance insulators, which are extremely sensitive to composition, temperature, pressure and environment.

The samples of composition $(La_{1-y}Pr_y)_{0.7}Ca_{0..3}MnO_3$ were prepared using ceramic method from solutions following controlled sintering. Synthesis specifics was described in the work..

For this samples nonstoichiometry on oxygen was experimentally investigated in different atmospheres ($He+O_2$) in temperature range (900-1300°C). The relationship between nonstoichiometry on oxygen and temperature of metal-insulator transition was discussed. A dependence of substitution of La to Pr on nonstoichiometry was not detected.
Temperature and heat of transition of metal-insulator were studied for samples with different «y», a correlation between these values was discussed.

All measured heat capacities were proximate to those calculated on basis of additivity.
The following methods were utilized: simultaneous TG-DSC, X-ray and wet chemical analysis.

The stability of the PdX molecules (X=groups IIIA and IVA elements)

Andrea Ciccioli, Giovanni Balducci,* Guido Gigli

Dipartimento di Chimica, Università di Roma La Sapienza, p.le A. Moro 5, 00185, Roma, Italy

*corresponding author. E-mail: balducci@caspur.it

As a part of our recent investigations of the thermodynamic properties of some intermetallic systems, both in condensed phase and in gas phase, constituted by a transition metal like palladium and a metal or semimetal of the block p, our interest has been focused on the species PdX with X element of groups IIIA and IVA. With the exception of some species reported in previous investigations these molecules remain largely uncharacterized.

Among the outcomes of our investigation the new heteronuclear molecules PdGa, PdIn, PdPb and PdSn were identified and studied. The gas-phase equilibria involving these species have been measured by KC-MS and the relevant data analysed by the second-law and third-law methods in order to determine their dissociation energies. Making use of a critical analysis of the literature data, in particular theoretical results recently made available, the dissociation energies and the thermodynamic properties of the corresponding homonuclear diatomics have been assessed.

Our experimental data and literature data for the dissociation energies have been compared to the values calculated from various semiempirical models and bonding energies trends of predictive value have been derived.

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High Temperature Properties of Polymer Derived Amorphous Si-C-N Materials

Christoph Konetschny, Ralf Riedel
Darmstadt University of Technology, Department of Materials Science, Dispersive Solids Group, Petersenstraße 23, 64287 Darmstadt, Germany

Novel polymer derived amorphous ceramic materials in the ternary system Si-C-N reveal excellent high temperature stability in terms of crystallization, oxidation and creep resistance [1, 2]. Preceramic polymer powder compacts can be formed with a green density > 98 % of the theoretical density [3]. The high green density is realized utilizing uniaxial warm die pressing. After pyrolysis crack free Si-C-N bulk ceramic materials were obtained exhibiting an open porosity below 2 vol%. Mechanical properties in particular hardness and fracture toughness were analyzed. An extraordinary high temperature creep resistance of the ceramic materials were determined performing compression creep tests [2]. Long term creep experiments showed creep hardening which is related to a change of the microstructure of the amorphous material. The glass transformation temperature of the Si-C-N ceramic is estimated to 1500 °C, which is in good correlation with the crystallization temperature of this type of material. The viscosity of the ceramic material at 1280 °C is analyzed to $1.3 - 5.0 \cdot 10^{13}$ Pa·s which is three orders of magnitude higher than the value of fused silica [4]. The preparation of nearly dense Si-C-N ceramic components results in a significantly decreased oxidation rate which will increase the life time of these class of materials in oxidative atmospheres. X-ray investigations performed after oxidation of Si-C-N samples up to 1650 °C in flowing air reveal the formation of a complete α-cristobalite layer. This behavior gives the possibility for in situ passivation during high temperature applications in oxygen containing atmospheres. The excellent high temperature properties of Si-C-N combined with its low solid state density ($\rho \approx 2.3$ g/cm^3) can be utilized for applications in the field of motor and turbine devices.

Literature:

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High Temperature Oxidation of Non-Oxide Silicon Based Ceramics

Hagen Klemm, Christian Schubert, Waldemar Hermel
Fraunhofer-Institute of Ceramic Technologies and Sintered Materials,
Winterbergstr. 28, D-01277 Dresden, FRG

Nonoxide silicon based ceramics such as Si_3N_4 and SiC or $MoSi_2$ are promising candidates for use as structural components at high temperatures between 1300 and 1500°C. Recently developed materials exhibit remarkably high mechanical properties at elevated temperatures; however their actual application is still limited by their insufficient long-term reliability under severe thermal, environmental and mechanical loading conditions. Especially after longer exposure at elevated temperatures, the major lifetime determining factors, such as creep or subcritical crack growth, are strongly influenced by the interaction of the material with the oxidative environment.

The present study is focussed on the oxidation behavior of nonoxide silicon based ceramics. Various ceramic materials (Si_3N_4 and SiC or $MoSi_2$ and composites) were examined after long term oxidation tests (up to 10 000 h) at 1500°C in ambient air. The oxidation mechanisms were discussed on the basis of a comprehensive chemical and microstructural analysis of the materials after the oxidation tests. The oxidation of all materials obeyed a nearly parabolic mechanism as the consequence of the formation of a protective oxidation layer of SiO_2. However, different characteristic oxidation processes at the surface and the microstructure were observed dependent on the chemical composition of the ceramic materials. The diffusion of oxygen into the material and its further reaction in the bulk of the material were found to be the most critical factors during long term oxidation. Microstructural changes occurred, which led finally to a degradation of the mechanical properties of the ceramics.

These damages in the microstructure of the materials can be significantly reduced by purposeful microstructural engineering. Using Si_3N_4/SiC- and Si_3N_4/$MoSi_2$-composite materials provides the possibility to improve the high temperature stability of Si_3N_4 as the consequence of a changed oxidation mechanism.

As a result of the investigations it is concluded that especially these Si_3N_4 composites offer a significant potential for long-term applications up to 1500°C, suggesting the use of these materials as structural ceramic components in advanced gas turbines.

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Carburization test method tailored for ethylene cracker tubes

Emil H. Edwin[a], Tore Arnesen[a], Stein Brendryen[a], Kari Enqvist[b], Gert I. Hugosson[c]
[a]Statoil R&D, 7005 Trondheim, Norway, [b]BOREALIS Polymers Oy, FIN-06101
[c]BOREALIS, S-44486 Stenungsund, Sweden

High temperature carburization of the tube material is the number one problem in thermal cracker operation. Unexpected shutdowns and welding problems decrease the on-stream efficiency and increase material costs. Carburized material also exhibit higher coking rates which shorten the on-stream time between two decoking periods. It is well known that the best protection against carburization is to have a well adherent, thin, self repairing scale with a high fraction of chromium (also silicon and aluminum). Calculations and tube examinations from industrial crackers show that the crackers are operated within the stability limits of Cr_2O_3 during decoking and pyrolysis operation. Examinations show that 2-3 year old tubes with intact oxide scale protection have insignificant carbon penetration. The Cr_2O_3 scale is thermodynamically unstable in the atmosphere used in gas carburization testing and also in pack carburization testing above 1080 °C. Thus, under these conditions chromium based scale protection is non existent and the carburization penetration profile is merely a result of the carbon solubility, carbon diffusion and the amount of carbide forming elements in the alloy. Pack carburization testing below 1080°C show very limited oxide protection compared to earlier studies with C^{14} tracer measurement on pre-oxidized alloys and experience from cracker operation. The ranking of different materials is generally the same for gas and pack carburization testing. Experience show that carburization in ethylene furnaces progress with an initial incubation period (protective oxide, very slow carburization) and a escalation period (non-protective oxide, excessive carburization rate similar to the rates in carburization testing). The carburization test method presented in this paper focuses mainly on the incubation time and the factors destroying the oxide layer during pyrolysis. The incubation time is also the most interesting period of the tube lifetime because the coke formation is low, the mechanical properties are good and the chance of extending the incubation period is good with respect to changes in the operational conditions.

The described carburization rig is a miniature cracker running sequential periods with pyrolysis of C_3H_8/H_2O (1050-1120°C) and air/steam decoking (1000°). The mechanisms of oxide degradation (oxidation, stress, carbon filament formation, erosion, Cr- evaporation, p_{O2} cycling) are outlined with some examples from industrial crackers. Some calculations are also presented. These degradation mechanisms are simulated and exited with a high frequency and with a certain intensification in the carburization rig. Carburization is achieved within 500 hours with thermodynamically stable Cr_2O_3 during the test period. All test samples are carefully pre-oxidized before exposure. Selected samples of HP alloy and 45/35 (Ni/Cr) micro alloy were tested in the rig. The tests show huge differences in carburization resistance between HP and 45/35 alloys. This is consistent with carburization measurements in the Borealis crackers while reported pack carburization tests show only minor differences. Significant carburization differences between alloys with similar compositions but from different producers are also presented (producer names are keep anonymous). Several previous studies have performed carburization testing in a simulated pyrolysis environment. However it seems that all of these works introduce periods with reducing atmospheres in respect to Cr_2O_3 stability.

COMPARATIVE STUDY OF THE REACTIVITY OF COPPER-NICKEL ALLOYS (ELECTRODEPOSITED AND ROLLED) AT HIGH TEMPERATURE IN PURE OXYGEN.

C. BERTRAND, A.L. DALTIN, J. DOUGLADE and S. TOESCA, DTI, EP 120 CNRS, Université de Reims Champagne-Ardenne, BP 1039, 51687 REIMS CEDEX 2, FRANCE.

The oxidation resistance of Nickel-Copper alloys Ni45Cu has been investigated between 600 and 1000°C under a pressure of 1 bar of pure oxygen.

The electrodeposited alloy was elaborated using a galvanostatic mode, from a bath containing 0.1 M of copper sulphate and 1 M of nickel sulphate. Sodium citrate (0.25 M) was used as complexing agent and sodium dodecylsulphate was added to avoid pitting phenomena ; pH was adjusted at a value of 8.9 and temperature at 20°C. The massic composition Ni45Cu has been obtained under a current density of 0.72 A / dm^2 with magnetic convection. The average specimen thickness was 50 μm and the alloy exhibits a columnar structure with a large grain size, which induces a rather high surface roughness. X-ray patterns indicate a structure with (111) preferential orientations.

The rolled Ni45Cu material was of Goodfellow origin.

The thermogravimetric analysis between 600 and 1000°C under a pressure of 1 bar of pure oxygen exhibits the following features:

-A noticeable oxidation rate is observed just above 600°C for the electrodeposited material, with a two-step process : a protective NiO layer is first developed and there is an acceleration involving the formation of copper oxide. At this temperature, the rolled material has a very low reaction rate.

-Between 700 and 800°C, a similar two-step kinetic phenomenon is observed with the rolled specimens since times of exposure to oxygen are not too long.

-At higher temperatures, a three-step mechanism may be noticed for all the samples ; the last step is characterised with a very low oxidation rate for the electrodeposited samples but, for the rolled ones, the final oxidation occurs very quickly.

-Except for transitory processes, kinetic laws are always parabolic and allow to compute activation energies.

At low temperatures, the electrodeposited material is much more oxidable than the rolled one : the columnar structure, the grain size and probably the additives of the electrolytic bath may be responsible of the lower resistance to oxidation.

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The control of the high temperature oxidation behaviour of precursor derived Si-B-C-N ceramics by pre-treatments?

E. Butchereit & K.G. Nickel
Eberhard-Karls-University Tübingen
Institute for Mineralogy, Petrology,and Geochemistry
Wilhelmstr. 56
D-72074 Tübingen

Precursor derived ceramics are obtained by pyrolysis of preceramic networks at temperatures as low as 1000°C. In contrast to sintered ceramics, these materials are X-ray amorphous and free of sintering additives. Both features do not only improve the mechanical properties but are also expected to benefit the oxidation resistance.

Oxidation experiments, which were [illegible] out in the temperature range between 1100 and 1600°C in both dry and moist oxygen using precursor derived ceramics, showed significant differences between boron free and boron containing samples. Ceramics in the system Si-C-N showed an increasing mass gain with increasing temperature and the formation of a dense protecting oxide scale after oxidation at 1500°C. After 36h at 1600°C growth of a multi-layered bubble-rich oxide scale was observed. In contrast, boron containing samples showed a decreasing mass gain with increasing temperature. Beginning bubble formation was already observed at 1100°C, resulting in irregular bubble-rich scales at higher temperatures. These results are in contrast to oxidation experiments at 1500°C in air carried out by Baldus et al. [1] using a $SiBN_3C$ ceramic, which resulted in the formation of a dense, double-layered $BN(O)/SiO_2$ scale.

To investigate how the oxidation behaviour of the boron containing samples can be controlled by thermal pre-treatment prior to oxidation, corresponding experiments were carried out in air and oxygen. The results will be reported and interpreted on the basis of thermodynamic calculations.

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High temperature electrochemical corrosion of steel 12Kh18Ni10Ti and its components in alkali carbonate melts at 500-650 °C

Kudyakov V.Ya., Domnin A.E., Perin S.M., Nikitina E.V.
Institute of high temperature electrochemistry, Kovalevskaya-street, 20, Ekaterinburg, Russia

Molten carbonate electrolytes are used in the new perspective branches of modern technology (high temperature sources of current, salts bathes for metals treatment etc). Corrosion resistance of metal materials in molten salts has important role to successful organization of carrying out different electrochemical devices. Investigation of corrosion process allows of the material choice and protecting its.

During interaction of metal materials with alkali carbonate melts single oxide nonstechiometric phase is formed. The latter separated metal and melt, and corrosion arises due to diffusion of the reagents throughout oxide layer. There are two methods to put the brake on process: preliminary injection small amount of elements into metal and doping of inhibiting addition into melt.

We investigate corrosion and electrochemical characteristics of the steel 12Kh18Ni10Ti and single components of it in mixed carbonate melt (40 molar percent of lithium carbonate, 30 molar percent of sodium carbonate, 30 molar percent of potassium carbonate). Corrosion of steel is examined under air atmosphere at 500-650 °C. Work and counter electrodes are steel wire with diameter 2,5 mm and surface area about 3 cm^2. As reference electrode we use carbonate-oxygen electrode.

Individual pure nickel, chromium, titanium (rectangular samples with area about 5 cm^2) are studied under atmosphere of carbon dioxide and oxygen in three-electrode cell. The counter electrode is platinum plate with area about 10 cm^2 . Sodium peroxide is injected into melt (concentration is varied from 1 to 7 molar percent). Crucibles are made from alumina.

We performed measurements of corrosion potentials, corrosion losses of mass, potentials and currents of passivation of metals materials. There are metallografic, atom-absorption, micro-X-ray spectroscopic, structure X-ray analysis.

Influence of steel components and inhibitors in melt to corrosion-electrochemical behavior of steel is explored.

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Oxidation of orthorhombic TiAlNb alloys at 800°C in air

A. Ralison, F. Dettenwanger, M. Schütze

Karl-Winnacker-Institut der Dechema e.V.
D-60487 Frankfurt am Main, Germany

Different TiAlNb compositions with various (-stabilising elements contents (Si, Mo, Ta) were investigated with respect to their oxidation resistance in air at 800°C. Weight changes and acoustic emission were measured during cyclic and continuous experiments. The oxide scales and the scale/metal interface were characterised using metallography, microhardness measurements, SEM and EPMA investigations. The orthorhombic alloys showed a severe spallation after several 100 h at 800°C in air, as a result of the formation of a non-protective AlNbO4/TiO2 multilayered scale. The respective oxidation kinetics could be correlated to the influence of the (-stabilising elements. The specimens were quite sensible to surface embrittlement. On all alloys the metal/oxide interface consisted of a mixture of oxides (Al2O3) and nitrides (mainly TiN). This interface was followed by an interstitial affected zone consisting of a graduated oxygen inward diffusion related to an inversely graduated Nb-enrichment. However, a remarkably protective oxide scale morphology could be observed locally after a 1000 h-experiment on the Ta-containing specimen. This was associated with a local Al, Ta, Nb enrichment and a decreased oxygen uptake. Indeed, no inward oxygen diffusion was observed at these locations and only a thin adherent oxide scale had developed. The metal/scale interface is being investigated further using XRD and TEM techniques and the beneficial effect of Ta will be discussed.

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High Temperature Corrosion of cobalt based intermetallic compound CoGa

U. Koops, M. Martin
Institute of Physical Chemistry Electrochemistry
Darmstadt University of Technology
Petersenstrasse 20, 64287 Darmstadt
HYPERLINK mailto:koops@e-chemie.tu-darmstadt.de koops@e-chemie.tu-darmstadt.de

The corrosion behavior of the intermetallic compound Co1-xGax, which is stable in the stoichiometry range of $0.29<x<0.64$ [1], was studied at moderately high temperatures (800°C) in air using x-ray powder diffraction and optical microscopy.

Selective oxidation of gallium to form (-Galliumoxide Ga2O3 is observed.

The growth kinetics can be deduced form the intensities of the x-ray powder reflections as well as from the interference colors of the thin oxide layer. Differently orientated grains in a polycrystalline disc reveal differently thick oxide layers after exposure. The oxidation rate is of the same magnitude as the growth rate of (-Al2O3 on NiAl.

During oxidation pores are formed in the metal surface of the metalloxide interface while the oxide layer remains smooth on both interfaces (metalloxide and oxidelgas). Detection of the pores was performed by optical microscopy through the transparent oxide layer and by scanning electron microscopy on cleaved and bent surfaces. The pores reveal rectangular shape according to the bcc-structure of the base intermetallic. Pore formation can be explained by the condensation of supersaturated vacancies which were chemically induced by selective oxidation of gallium.

The low growth rate of the formed oxide proposes good corrosion resistance at moderate temperatures in air, but the low melting point of 1207°C may prevent this material from industrial usage.

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Rhenium-Oxygen Interactions at High Temperatures

Nathan S. Jacobson
NASA John H. Glenn Research Center
Cleveland, OH 44135

Dwight Myers
East Central University
Ada, OK 74820

Dongming Zhu
Ohio Aerospace Institute
Brookpark, OH 44142

A novel satellite propulsion system involves passing highly concentrated solar energy through a secondary refractive oxide crystal (1). Candidate crystals include MgO, Al_2O_3, and ZrO_2. Solar energy is transferred from the crystal to a rhenium cavity which is heated to 2000K and in turn heats a propulsive gas. The crystal can reach temperatures of 2000K and hence the interaction of oxygen from the crystal and/or residual gaseous oxygen in the system with the rhenium cavity is important.

A recent assessment (2) and literature review of the Re-O system indicates the major vapor species are $Re_2O_7(g)$, $ReO_3(g)$, and $Re_2O_6(g)$. Two types of experiments were done. Re coupons in contact with MgO or Al_2O_3 were heated at 1500-1800°C in a vacuum. In addition Re coupons were reacted with various mixtures of O_2/Ar at temperatures of 1000°C.

Interactions of Re with MgO and Al_2O_3 are minimal with the Re acting as a mask in a Langmuir vaporization process. This suggests that the oxygen partial pressure generated from the decomposition of these oxides is too low to attack the Re.

In flowing O_2/Ar mixtures, substantial reaction rates are noted, depending on the partial pressure of oxygen. The measured rates are compared to those predicted from boundary-layer-limited mass transport of $Re_2O_7(g)$, $ReO_3(g)$, and $Re_2O_6(g)$.

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Oxidation Behavior of Y_2SiO_5/SiC Coating for C/C Composites

Y. Ogura, M. Kondo, T. Moromoto, Y.Takeda*, and A.Noutomi*
Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd., Yokohama 236-8515
*Nagasaki Research and Development Center, Mitsubishi Heavy Industries, Ltd.,Nagasaki 851-0392

C/C composites is favorable for high-temperature structural applications because of low density and superior mechanical strength at high temperature. Oxidation protection coating on C/C composites is indispensable for application in oxidizing atmosphere. SiC coatings could provide reliable protection below 1500Åé. One approach for improvement of reliability of SiC coatings at higher temperature is to apply an erosion resistant outer layer. Y_2SiO_5 is promising candidate materials for the outer layer, because it melts at 1980Åé, has little thermal mismatch stress on SiC layer, a low vaporizing rate and a low oxygen permeability.

The oxidation behavior of Y_2SiO_5/SiC coated graphite has been investigated. Y_2SiO_5 coating was produced by plasma spraying on CVD-SiC precoated graphite. Y_2SiO_5 coating improves oxidation resistance of CVD-SiC precoated graphite at 1700Åé under low total pressure. High temperature mass spectrometric analysis of the oxidation behavior indicates suppression of active oxidation rate of SiC layer by Y_2SiO_5 layer.

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Oxidation of innovative carbon based materials for future energy systems

H.-K.Hinssen, A.-K.Krüssenberg*, R.Moormann[1], C.H.Wu**
*Forschungszentrum Jülich/ISR, D 52425 Jülich; *Forschungszentrum Rossendorf FWSS, D 01314 Dresden, **NET/MPI-Garching, D 85748 Garching bei München*

Due to their excellent mechanical and thermal properties C-based materials are used in High Temperature (HTR) and Fusion Reactor concepts for basic components: Fuel elements and reflectors of HTRs are made from graphite and in Fusion Reactors parts of the plasma facing components within the vacuum vessel consist of C-based materials. Because of their limited oxidation resistance at high temperatures accidents, leading to contact of oxidising gases (air or steam) with these carbon components, have to be considered in safety analyses. In addition, strength loss of carbon materials due to oxidation by impurities in cooling gas is an important aspect for HTR normal operation; accordingly, selection of carbon materials has to take into account their oxidation resistance.

This paper gives an overview on theoretical work and measurements in Jülich concerning oxidation kinetics of selected innovative C-based materials (graphite, CFC) with and without doping in oxygen (523 - 1223 K) and steam (1100 - 1523 K). Also data and theoretical models on depth of penetration of the oxidation process are presented. Data on oxidation induced release of hydrogen isotopes from redeposited a-C:H layers on first walls in fusion reactors are outlined, too.

Futheron, fields of insufficient knowledge are identified: These include data for an improved oxidation model considering both in-pore diffusion and chemical reaction and data/models on catalytic oxidation. Also, a lack of data on the Boudouard reaction, which has to be considered in course of air ingress accidents, was identified.

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The Effects of Exposing Hot Pressed Silicon Nitride and Rare Earth Silicon Oxy-Nitride Phases to a High Temperature H_2S Rich Gas Environment

*†#M. O'Reilly, *J. Corish and †R..J. Fordham

*Department of Chemistry, Trinity College, Dublin 2, Ireland
†Institute for Advanced Materials, European Commission JRC, Petten, The Netherlands

Abstract

This paper reports on the effects of exposing hot pressed silicon nitride and a selection of rare earth silicon oxy-nitride phases to 0.4% H_2S/H_2 at 1573K. The silicon oxy nitride phases studied included cerium and neodymium apatites and cerium, neodymium and yttrium -N-α-wollastonites. Apatite and wollastonite phases are commonly present in the intergranular system of dense silicon nitride.

Previous studies have discussed the critical role which the various intergranular systems plays in enhancing the rate of oxidation of silicon nitride. The current study shows that in a reducing gas environment the grain boundary phases appeared to have little effect or influence on the rate of attack of the silicon nitride. They do however, undergo a series of complex reactions forming metal sulphides and metal oxy sulphides and these changes in chemistry are discussed.

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Stability of some potassium and sodium ferrites in relation to chloride-enhanced oxidation

Martti Makipaa* and Richard J. Fordham
European Commission, Joint Research Centre,
Institute for Advanced Materials,
PO Box 2, 1755 ZG Petten,
The Netherlands

State-of-the-art mechanistic explanations of chloride-enhanced oxidation of carbon and low alloy steels usually include a hypothetical reaction step where a "protective" oxide scale reacts with alkali chloride to form alkali ferrite and gaseous chlorine. To investigate these claims, accurate thermodynamic and kinetic data for reactions involving alkali ferrites are necessary. In the present study, experiments using a CAHN-thermobalance supported with X-ray diffraction, SEM/EDS and Hot-Stage Optical microscopy were used for this purpose. TG-curves were determined for various mixtures of iron (III) oxide with alkali carbonates and/or alkali chlorides under atmospheres of dry air and different CO_2-O_2-N_2 mixtures. Precise estimates of ΔG_r were calculated at various temperatures for reversible reactions. In the case of $KFeO_2$, experimentally determined values of ΔG_r showed that $\Delta G_f(T)$ data found in most major compilations for this compound are obsolete and erroneous. Any corrosion mechanistic analyses based on these values are thus largely misleading. Preliminary weight-loss experiments, performed elsewhere in ambient air, indicated that alkali carbonate-iron oxide reaction rates are greatly enhanced in the presence of alkali chloride. Further investigations were made to study this effect in detail under controlled atmospheres.

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* currently detached from VTT Manufacturing Technologies, PO Box 1703, Espoo, Finland, FIN-02044

High Temperature Corrosion of Ceramics against Coal Slags [*]

T. Karwath, P. Biedenkopf, E. Wessel, M. V. Rane, K. Hilpert, L. Singheiser
Research Center Jülich, D-52425 Jülich, Germany

D. Pavone
DKSF, c/o steag EBS, Halterner Str. 105, D-46284 Dorsten, Germany

K. Hannes
STEAG Aktiengesellschaft, D-45117 Essen, Germany

Gas cleaning related to fly ashes and alkali is a necessary prerequisite for the direct use of combustion gas in an advanced gas turbine system. In case of the pressurized pulverized coal combustion (PPCC) the flue gas is routed through a column of ceramic balls at an average temperature of 1500 °C before entering the gas turbine. The temperature of the formed liquid slag amounts to about 1450 °C. The slag flows down the column of ceramic balls.

However, the highly corrosive basic slag can react with the ceramic balls. Fly ashes in the liquid state contain high concentrations of SiO_2, Al_2O_3 and Fe_2O_3 which penetrate the refractory structure forming low melting eutectic mixtures. This work had the following aims:

- Elucidation of the mechanisms of corrosion attack of oxide ceramics by liquid slags.
- Investigation of the influence of the slag, which covers the ceramic surface, on the vaporization of chromium.
- Study of the influence of the composition of the ceramics on the vaporization of chromium.

Corrosion tests of eight Al_2O_3-Cr_2O_3 base ceramics were conducted at 1450 °C, each exposed to slag from a PPCC test facility. In addition, the vaporization of chromium containing ceramics was investigated by high temperature mass spectrometry.

The results of the corrosion tests are:

- Non-porous sintered chromia base ceramics of high density with a homogeneous distribution of the components show good corrosion resistance against basic slag attack.
- Under these conditions, the corrosion resistance increases with increasing chromium oxide content.
- The observed good corrosion resistance can be explained by the formation of the thermodynamically very stable spinel phase $MgCr_2O_4$ which forms a layer on the surface of the solid ceramics.
- The formation of the protective $MgCr_2O_4$ layer is thermodynamically forced by the presence of $MgCr_2O_4$ in the matrix of the Cr_2O_3 ceramics. In this case, a dense $MgCr_2O_4$ layer is formed on the ceramic surface.
- The presence of slag enhances the vaporization rate of chromium by formation of gaseous alkali chromates ($A_2CrO_4(g)$; A = Na, K) by the reaction of the alkali oxides (Na_2O, K_2O) from the slag with the chromium oxide from the ceramics. The chromium vaporization is even raised if the ceramics is completely covered by the slag.
- Pure Cr_2O_3 ceramics shows the highest and pure homogeneous $MgCr_2O_4$ ceramics the lowest chromium vaporization rate. A reduction of the chromium vaporization by a factor of 10 is possible by the absence of the Cr_2O_3 phase in the ceramics or by the complete covering of the ceramic surface by a dense $MgCr_2O_4$ layer.
- The chromium vaporization from mixed chromium oxide ceramics without liquid slag is a function of the chromium concentration, chromium distribution, diffusion rate of Cr in the solid phase, temperature, and of the bonding of the Cr^{3+} ion in the mineral phase.

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[*] This work has been supported by the German ministry of economics (BMWi) (Project 0326840A)

Post Deadline Posters C

C 1 – C 6

New thermodynamic measurements and assessment in the U-Fe system

D. Labroche, J. Rogez*, C. Guéneau** and O. Dugne
CEA-VALRHO, DCC/DTE/SIM, BP 111, 26702 Pierrelatte Cedex – FRANCE
* CTM, 26 rue du 141 ème RIA, 13003 Marseille - FRANCE
**CEA-SACLAY, DCC/DPE, 91191 Gif sur Yvette - FRANCE

The (U,Fe,O) system is one of the basic systems in the nuclear research. For example, the compounds of the ternary system i) can be used as additives in the fuel and also ii) constitute some wastes of the enrichment uranium plants. iii) The system constitutes one of the side system of the main (U,Zr,Fe,O) system the knowledge of which is essential in the safety nuclear program. The re-examination of the metallic part (U-Fe) of the ternary (U,Fe,O) is one of the first steps of the study.

Two line compounds, UFe_2 and U_6Fe, are described in the (U-Fe) system. UFe_2 melts congruently and U_6Fe presents a peritectic decomposition. Some lack and discrepancy are observed in the thermodynamic description of these compounds. The Gibbs energy of formation of the UFe_2 compound has been measured by Yoshihara and al. [1]. The enthalpy of formation of UFe_2 has been already determined by acid solution calorimetry [2-4], but the published values widely disagree with emf measurements. The enthalpy of formation of U_6Fe is unknown and no data are available for the heat capacities and the enthalpies of melting.

The aim of this study is first to measure a consistent set of thermodynamic data for the line compounds :

- The specific heats are determined by adiabatic calorimetry in the temperature range 700-1500 K. The melting enthalpy and the temperature of fusion of UFe_2 are measured by the same calorimetric method.
- The enthalpy of formation of UFe_2 and U_6Fe are measured by solution calorimetry at two temperatures : at 298.15 K in an aqueous acid solvent and at high temperature in a semimetallic bath.

The double determination of the enthalpies of formation added to the heat capacities of the compounds and the references allow to propose a set of coherent data for UFe_2 et U_6Fe.

The phase diagram is finally reassessed by means of the Thermocalc program and a new thermodynamic description is proposed.

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C2

Simulation of kinetics of ferrite growth in Fe-C austenite with interface of finite mobility.

Jiří Svoboda[1], Jiří Sopoušek[2]

[1] Institute of Physics of Materials, Academy of Sciences of the Czech Republic, □i□kova 22,
CZ 616 62 Brno, Czech Republic

[2] Masaryk University, Faculty of Science, Department of Theoretical and
Physical Chemistry, Kotlářská 2, CZ-611 37 Brno, Czech Republic

The transformation austenite -> ferrite spontaneously takes place in iron carbon based systems at temperatures under the transformation temperature. Nucleation of ferrite occurs at the grain boundaries and the layers of ferrite grow to the detriment of the austenite grains. With respect to our interest in formation of cracks during continuous casting we will study only the initial stages before the perlite is formed.

If the ferrite layer grows, interface migrates and carbon diffuses from the interface into the austenite grain. Both processes are heat activated ones and can be described thermodynamically. The situation can be described as a 1-D periodical problem.

The driving force for the transformation is due to the decrease of the chemical free energy in the system taken as the internal driving force and the decrease of the mechanical energy treated as an external driving force. Motion of the interface causes the flux of the carbon into austenite which must be compensated by the diffusive flux from the interface into the austenite.

The internal driving force of the interface migration is given by the total decrease of the free energy in the system when the interface is infinitesimaly moved, which can be evaluated e.g. by the program THERMOCALC.

If the internal and external driving forces are known, the problem of coupled migration of the interface and the diffusion of carbon can be solved numerically for various interface mobilities, carbon diffusivities and external and internal driving forces. The concentration profiles in austenite and the kinetics of interface migration can be determined.

The simulation represents the decisive step in the determination of transformation kinetics in steels.

C3

The Optical Properties of Liquid Cerium at 632.8 nm

R.I. Sheldon and G.H. Rinehart

Nuclear Materials Technology Division, Los Alamos National Laboratory, Los Alamos,

NM, 87545

S. Krishnan and P.C. Nordine

Containerless Research, Inc., 906 University Place, Evanston, Il 60201

Abstract

The normal, spectral emissivity, $\varepsilon_\lambda(T)$, and optical constants, n and k, of liquid cerium were measured at 632.8 nm over a temperature range of 1702 – 2171 K using rotating analyzer ellipsometry. The cerium was electromagnetically levitated and melted to prevent contamination of the liquid metal by contact with a container. The emissivity at 0.9 μ and 1900 K was determined from the brightness temperature. The solubility of oxygen in liquid cerium at 1786 K was estimated and the effect of oxygen on the optical properties was demonstrated. Using available thermodynamic data and assumptions of ideal solution behavior, the volatilization of oxygen and nitrogen impurities is discussed.

C4

Bond Energies of Ternary Transition Metal Carbides from Mass Spectrometric Equilibrium Measurements

G. Meloni and K.A. Gingerich

Texas A&M University, Department of Chemistry, P. O. Box 30012, College Station, TX
77842-3012, USA

The Knudsen cell mass spectrometry was employed to measure the equilibrium partial pressure of ternary transition metal carbides of cerium with rhodium or ruthenium over the Ce-Rh-Ru-Os-graphite system in the temperature range of 2327 - 2806 K. From the partial pressures and estimated thermal functions the enthalpies of pressure independent reactions such as:

$$MC(g) + CeC_2(g) = MCeC_2(g) + C(g) \qquad M = Rh \text{ or } Ru$$

$$\text{or} \qquad M(g) + CeC_2(g) = MCeC(g) + C(g)$$

have been determined. From these reaction enthalpies and ancillary literature data the following preliminary values for the atomization enthalpies, $\Delta_a H_0^o$, in kJ mol^{-1}, have been obtained: RhCeC, 998; $RhCeC_2$, 1725; $RhCeC_3$, 2340; RuCeC, 1100; $RuCeC_2$, 1730. The $\Delta_a H_0^o$ of $RhCeC_3$ is an upper value. These results have been achieved considering linear structures, M - C_n - Ce (n = 1-3).

The bond energies will be compared with literature values of other ternary transition metal carbides and discussed in terms of bond additivity concepts.

This work at Texas A&M University has been supported by the Robert A. Welch Foundation and the National Science Foundation.

C5

Knudsen-Effusion Mass Spectrometry Study of Tin Clusters: Sn_2 - Sn_7

K.A. Gingerich, R.W. Schmude, Jr.[a], J. E. Kingcade, Jr.[b], and G. Meloni
Texas A&M University, Department of Chemistry, P. O. Box 30012, College Station, TX
77842-3012, USA

The high-temperature mass spectrometric method has been employed to measure the equilibrium partial pressure of small tin clusters. These data were combined with new thermal functions for Sn_2 - Sn_7, calculated from recent literature theoretical and spectroscopic molecular parameters, to evaluate the atomization energies and enthalpies of formation of the tin clusters.

The atomization enthalpies, $\Delta_a H_0^o$, and enthalpies of formation, $\Delta_f H_{298}^o$, in kJ mol^{-1}, of Sn_2 and Sn_3 were taken from Gingerich et al., *High Temp. Sc.* **21**, 1 (1986). The following preliminary atomization enthalpies, $\Delta_a H_0^o$ (Sn_n, g), and enthalpies of formation, $\Delta_f H_{298}^o$(Sn_n, g), in kJ mol^{-1}, has been obtained: Sn_4, 743±22 and 458±22; Sn_5, 972±27 and 530±27; Sn_6, 1315±33 and 487±33; Sn_7, 1618±42 and 486±42.

The atomization energies and fragmentation energies of group IV clusters are compared and discussed.

This work at Texas A&M University has been supported by the Robert A. Welch Foundation and the National Science Foundation.

[a] Current address: Division of Natural Science and Nursing, Gordon College, 419 College Dr., Barnesville, GA 30204.
[b] Current address: Blinn College, Division of Natural Science, Brenham, TX 77833

C6

High temperature reactions for controlling the low temperature properties of $REBa_2Cu_3O_7$ based superconducting ceramics

Gernot Krabbes
IFW - Institute of Solid State and Materials Research Dresden, P.O.B. D-01171 Dresden

Below 90 K, bulk high temperature superconductor materials (HTSC, in form of ceramic discs, cylinders, rings etc.) can carry large persistent superconducting currents induced by an applied magnetic field. The interaction between persistent current and magnetic field results in both repulsive and attractive forces. The bulk superconductor can shield magnetic fields or trap a remanent induction even higher than 10 T. These properties are interesting for possible applications in self stabilising "smart" magnetic bearings, linear frictionless transport systems, permanent magnets. Key properties are high critical current density j_C and large size of the persistent current loops, but also sufficient mechanical strength to resist the high internal Lorentz forces.

To achieve optimized properties the material must contain a sufficient number of defects acting as pinning centres for the magnetic flux and it must be free of weakly superconducting grain boundaries.

We report aspects of the high temperature processing which influence materials genesis, composition and doping in the HTSC compound as well as the micro- and nanostructur of the ceramic material.

The fundamental process is the following reversible peritectic reaction the goal of which is a "single grain" material consisting of the superconducting 123 with small 211 inclusions:

$$YBa_2Cu_3O_{7-\delta}\,\mathit{(123)}\ \text{ç}\ \ a\,Y_2BaCuO_5\,\mathit{(211)} + b\,\text{Liquid} + c\,O_2\,.$$

Knowledge of phase equilibria is an important tool to choice process conditions to avoid grain boundaries and to generate a microstructure favouring the pinning of magnetic flux in the material. The influence of stoichiometry and different admixtures will be discussed with respect to carrier doping (influencing T_c) or formation of nanostructured precipitates (by decomposition in a metastable region) as well as with respect to enforced mechanical strength of the brittle ceramic material by segregation of ductile Ag particles in the body.

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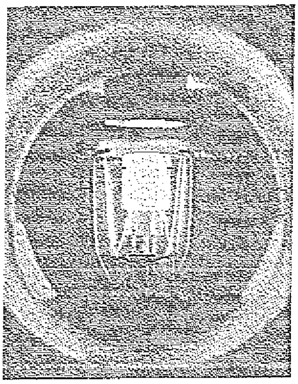

This book contains
the abstracts of the papers
presented at the
10th International IUPAC
Conference on
High Temperature
Materials Chemistry held
from 10 to 14 April 2000
at the Forschungszentrum
Jülich, Germany.

Forschungszentrum Jülich

Band / Volume 10
ISBN 3-89336-259-2

Energietechnik
Energy Technology