Materials for Advanced Power Engineering 1998

J. Lecomte-Beckers,
F. Schubert and P.J. Ennis (Editors)

Abstracts

UNIVERSITE DE LIEGE
EUROPEAN COMMISSION

Energietechnik
Energy Technology
Jacqueline Lecomte-Beckers, Florian Schubert and Philip J. Ennis (Editors)

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The provision of economical and reliable energy is a prime requirement for the success of manufacturing industry on which the well-being and standard of living of the population depend. Advanced power generation technologies seek to supply this demand for energy within the increasingly stringent economic and ecological restraints with respect to plant costs, fuel costs, fuel conservation and environmental impact. The key factor is the thermal efficiency of plant, which can be improved by increasing the temperatures and pressures of the processes. There is therefore a general requirement for improved materials and components which can operate reliably at higher temperatures and pressures.

The European Co-operation in the field of Scientific and Technical Research (COST) is a means for the co-ordination of national research programmes on a European level, COST actions consisting of basic and pre-competitive research. The Liège Conferences were initiated in order to disseminate the results of the materials related COST Actions, beginning with COST 50 which was mainly concerned with materials for gas turbines and then moving to COST 501 in which materials for power generation plant were investigated. The overall objective of COST 501, the results of which are reported in this Sixth Liege Conference, was to contribute, through a targeted programme of applied research, to the development of improved materials for advanced components in power engineering applications. The work was focused on topics concerning materials for the components that have a decisive influence on the enhancement of plant performance and efficiency, to ensure the ability of the European power engineering industry to remain competitive in the world market.

The critical materials and components in power generation plant have been identified and the required research and development activities have been based on the principle of work-sharing. Materials scientists, design engineers, alloy producers, component manufacturers, plant builders and plant operators have been brought together, reflecting the need to match materials properties and component behaviour. The power engineering systems covered include gas turbines (aero and stationary), steam turbines, diesel engines, fluidized bed combustors, gasification plant and waste incinerators.

The Conference comprised 6 invited lectures which put the materials research for advanced power engineering in a global context, 23 review papers that summarize the COST 501 activities and over 140 contributed papers presented as posters. The Conference Proceedings containing all the papers are organized as follows:

Part I: Materials for Advanced Steam Turbine Plant

Part II: Heat Exchangers and Fuel-Related Problems
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General Interest
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As in previous Liège Conferences, many people have made significant contributions to the success of this Conference. The excellent work of the members of the COST 501 Management Committee and the work package co-ordinators, who supervised and co-ordinated the research activities both in their respective countries and across the national borders, is highly appreciated. The editors would also like to express their gratitude to the other members of the Technical and Editorial Committee for their splendid work, 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.

September 1998

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Corrosion Resistant
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Gas Turbine:
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The 6th Liège Conference has been organized by the Forschungszentrum Jülich and the Université de Liège with the assistance of the Centre Recherches Métauxiques, Liège.
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C2 Gravill N., Benson J.M.*, McColvin G.**, Maldini M.*, Ross & Catherall (Great Britain), *CSIR (South Africa), **GEC Alsthom (Great Britain), *CNR-TeMPE (Italy)
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C9 Tamaki H., Yoshinari A., Okayama A., Nakamura S., Kageyama K.*, Ohno T.*
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Ecole Nationale Supérieure des Mines de Paris (France), *Turbomeca (France)
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C20 Neves S., Penkalla H.J., Schubert F., Singheiser L. Forschungszentrum Jülich (Germany)
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C25 Regina V., Remy L.*, Marchionni M.**, Guardamagna C.*
Volvo Aero Corp. (Sweden), *Ecole des Mines de Paris (France), **CNR-TeMPE (Italy), *ENEL/SRI (Italy)
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C29 Shemet V., Hoven H., Lersch P., Singheiser L., Quadakkers W.J.
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C30 Tomasi A., Gialanella S.*, Micheli V., Nazmy M.* *Istituto di Ricerca Scientifica e Tecnologica (Italy),
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RWTH Aachen (Germany), *National Physical Laboratory (Great Britain)
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**Ecole des Mines d'Albi-Carmaux (France), *MTU-Maintenance (Germany),
**Federal Institute of Technology (Switzerland)
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University of Minho (Portugal), *Forschungszentrum Jülich (Germany)
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University of Minho (Portugal), *Forschungszentrum Jülich (Germany)
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01 – 031
POWER ENGINEERING - STATUS AND TRENDS

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Abstract

The present power generation market is over 100 GW per annum, with coal fired steam plants and gas fired combined cycle power plants having the major share of around 35-40 GW per annum each. The major installations of coal fired steam power plants are in countries where natural gas is scarce (e.g. India, China) or where coal has been used traditionally in the past, e.g. USA and Germany. The growing power generation market with deregulation, privatization and environmental concerns has created a very attractive market for gas-fired combined cycle plants especially as natural gas is becoming widely available.

The Combined Cycle Power Plants (CCPP) and Combined Heat and Power Plants (CHP) offer the most attractive solutions to the operator, combining low installation cost and cost of electricity, with high performance and low emissions. Furthermore, the improvements in steam cycle and computational fluid dynamics have led to a significant increase in the efficiency of steam power plants. By adopting advanced steam conditions, improved economics and reduced emission of the coal fired plant will continue to be achieved. By the year 2000, a thermal efficiency of 60% for CCPP, and thermal efficiency of 48% for conventional steam power plants are realities. Advanced Cycle System (reheat gas turbine), modern water-steam cycle steam turbine / generator and controls are in place. For further progress and market success of the future power plants, the materials science and related manufacturing technologies with robust design and operation are the most important criteria.

Keywords: steam plant, combined cycle, efficiency, plant design
ENERGY AND ENVIRONMENT
(WISHFUL THINKING AND REALITY)

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Abstract
The rapid increase of economic wealth has been achieved by the invention of powerful technologies and by the ample availability of cheap fossil fuels. However, burning too much fossil fuel leads to the risk of global climate change, severely endangering life conditions on earth. On a time scale of decades the contribution of energy sources other than fossil fuels, such as renewable and nuclear energy will be rather limited not least because of their relatively high investment costs. Therefore the efficiency of present day energy technologies has to be improved as much as possible.
Advanced High Efficiency Steam Power Plant

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Abstract
There is a worldwide trend to higher efficiency power plant, both in order to reduce CO₂ emissions and to maximise benefits for power plant operators and customers by reducing lifetime costs. In this process it is necessary to consider a wide range of fuel choices and power plant options. Main and reheat steam temperatures have been increasing for recently commissioned steam power plant in Japan and Europe. Information on plant on order shows that this trend will continue into the next century both for conventional fossil fueled plant and combined cycle plant.

New materials for these applications have been developed in collaborative projects, such as COST, EPDC and EPRI, and many of these are now in use at temperatures up to 600°C. Manufacturing and operating experience have been good. Further steps are being taken in the COST 522 Programme (625-650°C) and in the Thermie Project (700°C).

It is intended that these projects should lead to the design of steam power plant with:
* reduced first-time costs (lower investment costs for a fixed MW output) and
* lower lifetime costs (lower overall cost of electricity)
HIGH TEMPERATURE FORGED COMPONENTS
FOR ADVANCED STEAM POWER PLANTS

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Abstract

Improved ferritic steels are required to minimize the costs for high temperature steam power plants and to provide high flexibility of operation (2 shift operation, frequent start-up/shut down). For this reason there are worldwide activities in research and development for the 9-12%CrMoV materials class. In Europe steel companies, turbine and boiler manufacturers, utilities and other users, testing institutes and universities worked together within the joint program COST501. The development goals in terms of required material properties, fabrication techniques (forging, casting, welding) and non-destructive examination had been defined by the turbine and boiler manufacturers. The alloy development work began in Round I in 1986 for 600°C materials, and Rounds II and III have continued the co-operation. In Round III the determination of the long term properties for the trial rotors E, F and B for 600°C application was one major point. The results show that the long term behaviour of the rotors is excellent.

On the other hand new trial melts (100-500kg) for 620/630°C application were made on the basis of new alloying concepts such as addition of Cobalt and Boron. The two different alloying concepts introduced by the group are basing on combinations of either Mo+Co or W+Co and Boron, Nitrogen and Niobium. Between the new chemical compositions tested here are promising alloys showing good results after creep testing times of about 15,000 h. Today it is not possible to favour clearly one of these concepts. For this reason the long term testing has to be continued.

The COST501 program was finished in December 1997. Future research will be treated under the new COST522 action which will start at the end of 1998.
HIGH TEMPERATURE CAST COMPONENTS FOR ADVANCED STEAM POWER PLANT

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Abstract

The development of ferritic-martensitic steels for advanced steam plants with steam admission temperatures in the range of 600 - 650 °C and super-critical steam pressure is of major importance because casting constitutes the most appropriate and economical manufacturing technique due to the complex design of the turbine casings and valve chests of the VHP, HP and IP turbines. The consequence is, in terms of weight and costs, a dominating cast steel proportion of around 60 % for the components of the VHP, HP and IP turbines.

Based on the results of development work on the P 91 cast steel grade G-X12CrMoVNbN 91, which were obtained under the EPRI Project 1403-15, COST 501 concentrated on developing and qualifying a tungsten-bearing cast steel grade. Test results have so far been obtained up to approx. 50,000 hours. In the long-term range at 600 °C the creep strength of this tungsten-bearing cast steel shows maximum conformance with the creep strength of P 91.

The newly developed cast steels G-X12CrMoVNbN 9 1 and G-X12CrMoWVNbN 10 1 1 are already used in 12 new European power stations with inlet temperatures up to 600 °C. The experience gained in the production of more than 350 castings in the weight range up to 60 t for these and other power stations is decidedly positive. The aim of current and future tests is to achieve inlet steam temperatures of up to max. 650 °C while continuing to use mainly ferritic-martensitic steels for turbine casings.
European Collaborative Evaluation of Advanced Boiler Materials

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Abstract
There are several R & D activities worldwide for the 9 to 12% Cr class of steels since they offer a potential of application under advanced operating conditions in modern steam power plants. In comparison to austenitic materials the extended use of ferritic steels will minimize the cost of investment and enhance the flexibility in operation both resulting in more economic energy generation.
In Europe boiler and turbine manufacturers, steel producers, utilities and testing institutes collaborated within the frame of COST501 to develop, evaluate and qualify advanced 9 to 12%Cr steels for applications in the 600 to 620°C temperature range.
Based on promising results with a W modified 11%Cr steel for rotor application in the 1st and 2nd round of COST501, a similar composition for boiler application was investigated by the boiler & welding subgroup in the 3rd round. This 1%W modification of the established P91 is designated E911 and was produced and tested in various product forms. There is a large database generated for E911 in COST, which is sufficient to apply for ASME/ASTM code approval. Components from the new E911 steel are already in service in operating power stations and will also be used in advanced plants currently under construction.
In order to serve as a comparison to E911 but also to get experience with the fabricability and the properties various products were also manufactured and tested from steel P92.
THE ROLE OF WELDING FOR COMPONENTS MADE FROM ADVANCED 9-12% CR STEELS

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Abstract
COST 501, Round 3, Working Package 11 “Welding Subgroup” developed 15 individual programs to determine quantitatively the influence of different welding procedures, welding parameters, welding consumables and post heat treating parameters on the mechanical, creep, LCF and toughness properties of welds on various advanced tungsten modified 9% Cr-steel. Base materials, weld metals and different dissimilar welds were investigated. Actual results of these investigations will be presented. Basically the weldability of these steels can be described as satisfactory. A soft zone in the weld connection negatively influencing the creep behaviour of welded joints was detected and was localized in the intercritical zone of the heat affected zone, limiting the long time creep strength of similar and dissimilar metal welds. The results obtained by the co-operative programme impressively showed that only by a full understanding of the mechanisms occurring in the microstructure of the welded joint successful measures can be applied to the selection of the welding material specification, the welding process and parameters and the postweld heat treatment procedure to increase the strengths, reliability and safety of these components.

Keywords: weldability, mechanical properties, creep properties
THE OXIDATION BEHAVIOUR OF FERRITIC AND AUSTENITIC STEELS IN SIMULATED POWER PLANT SERVICE ENVIRONMENTS

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Abstract
The high creep rupture strengths that can be achieved in the newly developed 9-12% chromium steels strengthened by additions of V, Nb, N and W enable the steels to be considered for applications in advanced fossil fuelled power generating plants operating at steam temperatures up to 650°C. The oxidation resistance of these steels, however, may be the factor that limits the temperature of operation, the formation of thick scales leading to over-heating of tubes due to the thermal insulation effect and loss of load-bearing cross-section leading to an increase in the creep rate and eventual creep failure. The significant parameters are the rate of scale formation and possible spalling of the scale, and the initial wall thickness of the component under consideration. The oxidation behaviour strongly depends on the \( \frac{H_2O}{O_2} \) ratio of the service or test environment; at high \( \frac{H_2O}{O_2} \) ratios, the oxidation rate is high. Under these conditions and for thin-walled components of below around 6 mm, the 9% Cr steels offer no significant advantage in service life over the 12% Cr steels with Cr contents near the top of the specified range (above about 11%).

Keywords: steam plant, 9-12% Cr steels, austenitic steel, high temperature oxidation, hot corrosion, gaseous corrosion.
PROGRESS IN UNDERSTANDING
MICROSTRUCTURE-PROPERTY RELATIONSHIPS
IN ADVANCED 9-12%Cr STEELS

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Abstract
COST 501 has been an important framework for alloy development for the power generation industry, especially in the area of high creep strength 9-12%Cr martensitic steels. Mechanical test programmes carried out on experimental alloys have generated a valuable archive of material for microstructural investigations. A collaborative effort by the COST 501/3 WP11 Metallography and Alloy Design Group has exploited this resource. As well as microstructural description, the project also incorporated development of models to predict microstructure and creep strength. The objective of this work was to improve understanding of microstructural evolution in these alloys, to relate microstructures to observed mechanical properties, especially creep strength, and to gain insights to facilitate development of improved materials. The scope of this activity, including efforts to quantitatively define the microstructures observed and some of the difficulties encountered in this area, is described. Recent achievements outside the project are also discussed. Insights valuable to future alloy development have been achieved, but significant limitations to application of the metallographic and modelling approach remain. Strategies to refine this approach and to create more powerful tools for alloy design are proposed.
MICROSTRUCTURAL STABILITY OF 9-12%CrMo(W)VNbN-STEELS

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Abstract
The microstructural stability of new 9-12%Cr steels during creep is discussed based on new findings with thermodynamic modelling and creep modelling. Dislocation and subgrain microstructures develop as a function of creep strain, and precipitate microstructures develop as a function of time. The precipitates interact with dislocations and subgrain boundaries, and control the development of strain in time. This means that the precipitate stability governs the creep strength of 9-12%Cr steels. Modelling of particle coarsening show that the coarsening rate of M23C6 carbides is determined by the Mo content of the steel and by diffusion of substitutional elements. Diffusion in ferrite of 9-12%Cr steels at app. 600°C is controlled by the Curie temperature, which is dependent on steel composition. Ni, Si, Mn and Cr accelerate diffusion and Co and C retard diffusion in 9-12%Cr steels. Based on the particle coarsening model it may be stated that Boron improves the creep strength in 9-12%Cr steels mainly by lowering the diffusion rates in the steels. Coarsening of the MX nitrides and Laves Phase is expected to be slow, but as these phases precipitate during creep, nucleation and growth plays a more important role in the creep strengthening effect, which can be achieved by MX and Laves Phase during long term creep.
FACTORS AFFECTING THE QUANTITATIVE EVALUATION OF MICROSTRUCTURES IN 9-12%Cr MARTENSITIC POWER PLANT STEELS

A Strang

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Abstract
A major part of the European COST 501 programme during the past 10 years has been directed towards the development of advanced 9-12%Cr martensitic creep resistant steels for high-temperature applications in high efficiency steam turbines. In addition to the assessment of the mechanical properties of these materials, a parallel activity has concentrated on the evaluation of their microstructures in both their original heat-treated condition and following long-term creep exposure at temperatures of 600°C and above. This activity was undertaken to provide a better understanding of the evolution of the microstructure of these steels resulting from high-temperature creep exposure and to provide quantitative data on certain key microstructural parameters to enable improved models for the prediction of their long-term properties to be developed. Since however the programme of microstructure evaluation was collaborative, an additional programme of Round Robin studies was initiated to determine the extent of interlaboratory scatter and assess its effects on the results of the microstructural parameter measurements. This involved particle size and subgrain size measurements being conducted on common samples by 11 laboratories within the group. The results of these Round Robin studies are presented in this paper and the main sources of interlaboratory scatter are identified. In addition procedures and practices are proposed to minimise the degree of scatter in future collaborative programmes in which quantitative metallography is a key feature.
MATERIALS REQUIREMENTS FOR ADVANCED
COAL FIRED POWER GENERATION TECHNOLOGIES

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Abstract

European industry is involved in the manufacture and use of all types of advanced fossil fuel
fired power plant. In recent years significant efforts have been directed at improving the
efficiency and thus reducing the environmental impact of power systems through the use of
higher efficiency steam and gas turbines. Boiler, heat exchanger, gas cleaning and other
system components need to keep pace with these developments if these high efficiency
systems are not to be restricted to 'clean' fuels at a time when the diversity of fuels
available for use in power plant has never been greater.

This paper looks at the challenges facing the developers of these components as they strive
to meet the reliability standards set for steam and gas turbines. In particular, the operating
environments and materials requirements for the components used in advanced coal
gasification systems will be reviewed. The components considered will include fuel gas
coolers, hot gas filters, hot gas desulphurisation systems, other gas cleaning stages and the
gas turbines required to handle the combustion products from the fuel gases produced.
Particular attention is paid to the effects of fuel constituents.
COAL GASIFICATION FOR POWER GENERATION: MATERIALS STUDIES

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Abstract
Current European activities on materials for coal gasification are described, with particular emphasis on the activities carried out in COST 501 Round III. Components targeted in these activities include fuel gas coolers as well as the range of parts needed in and downstream of hot gas cleaning systems. Increasingly realistic laboratory tests are being developed to simulate correctly the behaviour of materials in operational plants, including isothermal gaseous corrosion and downtime corrosion, as well as the effects of thermal cycles, deposits and stressing. One activity has concentrated on the development of predictive models of the performances of candidate materials. The forms of these models are compared with those of other research groups currently developing predictive materials performance models for reducing conditions. The validity of the COST models was shown by comparing predictions of the performances of materials in pilot plants with measurements of actual materials performances in the plants.

Keywords: materials issues, gasification, desulphurisation, downtime corrosion, modelling
MATERIALS FOR WASTE INCINERATORS AND BIOMASS PLANTS

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Abstract
This paper reviews the projects of the sub-package on waste incineration and biomass firing, carried out within COST 501, Round III, Work Package 13. The corrosive effects of incinerator and biomass combustion gases and deposits on heat exchange surfaces are well known. With regard to the complex environment, further laboratory based and long term plant evaluations were necessary to predict the corrosion behaviour in existing and future plants. The projects in the sub-package have covered the corrosion behaviour of candidate alloys and coatings with respect to life time predictions and the applicability of advanced steam conditions. Basic mechanisms of corrosion and the effect of impurities, in particular for components of biomass fired boilers, were studied.

Keywords: corrosion, waste incineration, biomass, superheaters, resistant alloys.
PRACTICAL EXPERIENCE IN THE DESIGN AND
OPERATION OF AN INDIRECT FIRED GAS TURBINE
PLANT USING AN ODS FERRITIC ALLOY HEATER

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Abstract

The paper describes the design, construction, and operation of a small scale, natural gas
fired heater, using ODS ferritic alloy tubing, for a demonstrator 1 MW_th Closed Cycle Gas
Turbine system. The design of the heater was of the "Harp" type. This was dictated by the
limited size and shape availability of both ODS alloy tubing and cast stainless steel header
materials, and the difficulties of using fusion welding with ODS alloys. Peak metal
temperatures on the tubing were 1150°C. The paper also briefly reviews related work with
ODS alloy development and understanding. It is considered that it would be possible to
construct an indirect fired or advanced steam turbine system, based on an ODS ferritic alloy
heat exchanger, using coal as a fuel.

Key words: Heat Exchanger, Closed Cycle Gas Turbine, High Temperature, ODS Alloy,
Oxidation, Nitridation, Embrittlement, Dissimilar Metal Joints.
NEW DEVELOPMENT IN LAND-BASED GAS TURBINE TECHNOLOGY

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Abstract

Application of aero-engine technology to land-based gas turbines has improved their power output and efficiency by a revolutionary step. The new Siemens gas turbine V94.3A includes these technologies after a successful cooperation with Pratt & Whitney. Future trends in cooling technology of land-based gas turbines will concentrate on minimization of leakage, effective use of cooling air and substitution of air by steam, to solve the problem of maximization of turbine inlet temperatures while minimizing combustor flame temperatures. Materials for combustor and turbine components shall allow to increase material temperatures without giving up any of the high strength properties. Single crystal alloys and thermal barrier coatings have been introduced now successfully to land-based gas turbines. Future technologies shall concentrate on ceramics for thermal insulation of combustors as well as for turbine airfoils.

Keywords: gas turbine, application, cooling technology, ceramics, combustor, turbine
THE CHARACTERISATION OF THE SINGLE CRYSTAL SUPERALLOY CMSX-4 FOR INDUSTRIAL GAS TURBINE BLADING APPLICATIONS

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Abstract
The use of single crystal (SC) superalloys in advanced blade designs of industrial gas turbines (IGT) is widely regarded as necessary in order to achieve the required increases in firing temperatures. However, the inherent anisotropy in these materials, as well as the anisotropy occurring due to microstructural changes after high temperature exposure, pose significant difficulties in the design assessment of components. The comprehensive characterisation of a candidate SC superalloy is therefore an important first step in understanding its deformation and failure behaviour, including the microstructural aspects of relevance to life prediction, and hence to provide the information required in the development of advanced design assessment methodologies. Preliminary data for the commercially available SC superalloy CMSX-4 have shown that it offers up to a 70°C advantage over traditional conventionally cast alloys and can be used in IGT provided it is coated in order to withstand the aggressive operating environment. A major part of the work of the SC Subgroup, Work Package 14 of the COST 501 programme has therefore concerned the characterisation of CMSX-4 in accordance with the above objectives. Emphasis was placed in understanding the behaviour of CMSX-4 in loading and temperature regimes of relevance to IGT applications and also in examining pertinent aspects of its behaviour, such as the strain rate sensitivity of the monotonic/cyclic deformation and failure, the anisotropy of the creep behaviour, and the interaction of creep - LCF and creep - HCF loadings.
DEFORMATION MODELLING OF THE SINGLE CRYSTAL SUPERALLOY CMSX-4 FOR INDUSTRIAL GAS TURBINE APPLICATIONS

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Abstract

Single crystal superalloys (SC) are actively being considered for use in industrial gas turbines (IGT) and it is therefore necessary to address the development of design assessment methodologies in parallel with the characterisation of candidate alloys. Previous design practice, as applied to conventionally cast components, involved a combination of simplified design methods and inelastic Finite Element (FE) analyses, particularly in cases where the predictions of the former were found to be too limiting. However, due to the anisotropy of the material response, the structural analogies used to support existing simplified methods are no longer applicable and inelastic FE methods are considered as essential in the prediction of life of SC components. A number of the activities of the SC Subgroup of Work Package 14 therefore concerned the development of material models which can be used to predict the anisotropic deformation behaviour of the commercially available alloy CMSX-4 in the temperature range 750°C to 950°C. The present paper discusses first several relevant issues concerning the design assessment of single crystal components and then proceeds to examine two deformation models which have been developed in the SC Subgroup. Emphasis has been placed in modelling aspects of the deformation which are relevant to IGT, in particular the anisotropy of the creep deformation and the evolution of rafting.

Keywords: design assessment of blades, anisotropy of creep behaviour, deformation modelling of CMSX-4, rafting in CMSX-4
THIRD GENERATION SUPERALLOYS FOR SINGLE CRYSTAL BLADES

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Abstract

The development of the single crystal (S.C.) blade casting technology has authorised the design of new nickel based superalloy chemistries suitable for this manufacturing process. These S.C. blades are now currently used within the most advanced gas turbine engines for civil and military aircrafts and helicopters. The first generation single crystal superalloys developed at the beginning of the eighties were originally derived from polycrystalline superalloys such as Mar-M247 which was the precursor of the CMSX-2 and CMSX-3 S.C. alloys developed by Cannon-Muskegon Corporation. Within the same period, the S.C.alloys PWA1480 and René N4 were developed in the USA respectively by Pratt & Whitney Aircraft and General Electric, the alloys SRR99 and RR2000 were designed by Rolls Royce in Great Britain, and the alloys AM1 and AM3 were developed in France.

A significant improvement of the mechanical properties of the single crystal superalloys, especially their creep strength, was then obtained due to the development of the so-called second generation S.C. superalloys. The main feature of these new alloys was that they contained about 3wt.% of rhenium. The principal advantage of rhenium is to slow down the coarsening rate of the strengthening γ phase precipitates during high temperature creep and hence to improve the stress-rupture life. On the other hand, these rhenium additions increase the density of the alloys compared to the 1st generation materials, render these materials more prone to the precipitation of brittle intermetallic phases topologically close-packed (TCP) phases and make the alloys much more expensive. Typical examples of 2nd generation S.C. alloys are PWA1484, René N5 and CMSX-4. An other criterion could however be selected for the definition of these 2nd generation alloys, based on the high temperature creep strength. In these conditions, the MC2 superalloy developed by ONERA is an integral part of this group, in spite of the fact that it does not contain rhenium. It is also a cheap alloy.

More recently, alloy designers tried to improve again the high temperature capability of the S.C. blade alloys by increasing the content of rhenium up to about 6 wt.% in. third generation alloys. The challenge was to achieve higher creep strengths, without increasing the density and by keeping the alloy not too much prone to the precipitation of TCP phases. The high level of refractory elements such as tungsten and rhenium may be also a drawback for these alloys, in terms of castability of S.C. components. Typical 3rd generation single crystal alloys are René N6 and CMSX-10 alloys. Other 3rd generation alloys are also today developed in different parts of the world. As an example, a family of new generation single crystal superalloys are under development at ONERA, showing competitive overall properties compared to the U.S. alloys.

A critical review of the approach for the development of these third generation S.C. alloy is made, trying to identify the advantages and drawbacks of this new family. This will allow us to judge the importance of these new materials in the context of aeronautical and industrial applications.
DISC MATERIALS FOR ADVANCED GAS TURBINES

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Abstract
Recent development trends for single and combined cycle gas turbine power plant are highlighted. Problems related to design, materials selection and manufacture of gas turbine rotor discs are discussed. Increased size and temperature level give rise to increased centrifugal and thermal stresses. These loads are assessed in terms of burst, low-cycle fatigue and crack growth (defect tolerance). The limitations of ferritic steels and the opportunities and risks involved in using austenitic alloys in discs for large industrial gas turbines are discussed. Aero-engine disc technology is reviewed and its potential in connection with industrial gas turbine discs is considered.

Keywords: industrial gas turbine, aero-engine, gas turbine disc, centrifugal stress, burst speed, thermal stress, low-cycle fatigue, fatigue crack growth, creep crack growth, ferritic steel, iron-base alloy, nickel-base alloy.
GAMMA TiAl INTERMETALLIC FOR GAS TURBINE APPLICATIONS

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Abstract

Gamma titanium aluminide intermetallics possess a unique combination of properties such as low density, high stiffness and good high temperature strength. This combination of properties is beneficial to a variety of components in gas turbines. For example, the application of gamma TiAl base material as a lightweight blade in the last stage blading will result in lower centrifugal stresses, in turn, will permit the use of larger blades which lead to improved efficiency and power output.

In the framework of COST 501/III WP14 sub-task Gamma TiAl, an extensive effort has been carried out to evaluate the different aspects of physical and mechanical properties of the ABB patented cast alloy Ti-47Al-2W-0.5Si.

In the present paper, an overview is given on the different types of the evaluated properties of this duplex microstructure material consisting of mainly lamellar $\gamma/\alpha_2$ and globular $\gamma$ grains, and small amounts of $\beta$ and Ti$_2$Si$_3$ silicides.

The evaluation of mechanical properties, specially at high temperature, showed that:

- The $\gamma$-TiAl material exhibited improved density corrected tensile and creep strengths as compared with the IN738LC Ni-base superalloy. Nevertheless, the tensile ductility of the $\gamma$-TiAl material was lower than that of IN738LC. In addition, the $\gamma$-TiAl, due to its low density, exhibited higher specific stiffness than that of IN738LC.
- The LCF properties of the $\gamma$-TiAl at 600 and 700°C was comparable with those of IN738LC.
- The HCF behavior was characterized by a different behavior than that of IN738LC: (a) less steep S-N curves and (b) high ratio of the endurance limit / ultimate tensile strength.
- The fatigue crack propagation behavior exhibited lower fracture toughness compared to IN738LC and an environmental effect balanced by a stress relaxation effect at high temperature.
- The oxidation and corrosion resistance of the $\gamma$-TiAl material showed improvement over those of IN738LC. Nevertheless, a protective coating is essential for the $\gamma$-TiAl at temperatures >700°C.
- On the basis of the findings of this evaluation activity, one has to take into consideration the gradients of microstructure, and hence of properties, existing in cast $\gamma$-TiAl components.
CONSIDERATIONS ON SOLIDIFICATION PATHS AND DEVELOPMENT OF NEW CASTABLE GAMMA TITANIUM ALUMINIDES

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Abstract

This paper deals with new cast gamma titanium aluminide alloys developed at ONERA, based on examinations of the role of solidification paths. While most of the alloys previously identified solidify through $\alpha$ showing an as-cast microstructure characterized by the presence of columnar $\alpha$ grains in which all the $\gamma$ lamellae are formed perpendicularly to the axis of these grains, our alloys solidify through $\beta$, the initial $\beta$ grains being divided into differently oriented colonies of $\alpha$ platelets in which $\gamma$ lamellae are subsequently formed. Although both categories of alloys show a $\gamma+\alpha_2$ lamellar structure, the new $\beta$-solidification alloys exhibit much less texture and smaller grain size than the $\alpha$-solidification alloys such as Ti-48Al-2Cr-2Nb. Mechanical tests conducted on the new alloys such as Ti-46.6Al-2Re-0.8Si, without any specific optimization of heat treatments, suggest that they show a reasonable room-temperature tensile ductility, together with an excellent high temperature creep strength.

Keywords: Intermetallics, TiAl, Cast alloys, Alloy development
THE EXPLORATION OF PROTECTIVE COATINGS AND DEPOSITION PROCESSES FOR NICKEL-BASE ALLOYS AND GAMMA TITANIUM ALUMINIDES

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Abstract

Three projects contained within Work Package 15 of COST 501 Round 3 were concerned with the development and evaluation of more durable protective coatings and the associated deposition processes for gas turbine components manufactured in nickel base alloys and titanium aluminate materials. The aim of the work was to study the relative merits of a wide range of thermal spraying, physical vapour deposition and chemical vapour deposition techniques for the deposition of unique oxidation resistant coatings containing noble metal/oxidative element additions and, or non-metallic strengthening phases, and to subsequently evaluate the mechanical properties and corrosion and oxidation resistance of the most promising candidates. The deposition processes included high velocity oxy-fuel spraying, reactive gas plasma spraying, electron beam evaporation and magnetron sputtering and the coatings ranged from the more extreme platinum aluminate compositions to complex overlay coatings with and without non metallic thin film diffusion barriers.

Keywords: coatings, platinum aluminides, MCrAlY's, intermetallics, mechanical properties, corrosion.
THERMAL BARRIER COATINGS FOR GAS TURBINE APPLICATIONS - FAILURE MECHANISMS AND LIFE PREDICTION

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Abstract

Typical properties of thermal barrier coatings (TBCs) for industrial gas turbines as well as aero engines are described. The coating deposition process parameters have to be controlled carefully to reduce the wide scatter of physical and mechanical properties reported in the literature. Typical failure mechanisms of TBCs are described, which can be attributed to high residual stresses resulting from the manufacturing process. Oxidation of the bond coating affects significantly long-term behaviour of TBCs resulting in spallation of the alumina scale. Superimposed mechanical stresses promote crack formation under tensile strains higher than 0.5 % and spallation under compressive stresses. Sintering effects of TBCs above 1000 °C increase Young’s modulus of the TBCs and results in phase changes above 1150 °C of the TBC. Service performance evaluation indicates that spallation of EB-PVD coatings primarily occurs by buckling of the alumina scale formed between the bond coat and the TBC.

Keywords: TBCs, physical properties, mechanical properties, EB-PVD, APS, MCrAlY, alumina scale, Ti additions, coefficient of thermal expansion
LIFETIME AND DEGRADATION PROCESSES
OF TBCs FOR DIESEL ENGINES

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Abstract
Development of Thermal Barrier Coatings (TBCs) for diesel engines has attracted great interest to improve engine efficiency and reduce emissions as well as fuel consumption. The following contribution includes a discussion about the effects of TBC use in combustion zone of diesel engines. Different degradation mechanisms working on TBC system in diesel combustion environment will be explained. The very different requirements to a TBC system demand a tailored approach of materials development, process control and engine testing. Spraying of thick TBCs on large components with evident long process times requires on-line process control for efficient processing, reproducibility and quality assurance. A multi-disciplinary approach of materials science, process engineering and component testing will be reviewed.
THE IMPACT OF MATERIALS RESEARCH FOR ENERGY TECHNOLOGIES PROVIDING FOR THE TWENTY-FIRST CENTURY

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Abstract

The research and development of materials for advanced power generation systems aim to provide materials and components that can operate under the increasingly demanding service conditions imposed by new energy technologies. For fossil fired plant the applied research work for the production of transpiration-cooled gas turbine components is described. The physical principles behind the newly emerging fuel cell technology are summarized and the materials research for the high temperature Solid Oxide Fuel Cell (SOFC) is discussed, with emphasis on the interface problems and long-term stability. The physical principles for nuclear fusion, demonstrated for Tokamak (ITER) and stellarator (Wendelstein 7-X) facilities illustrate the severe loading imposed on the plasma-facing components. The emphasis is given to the impact of heat flux exposure and neutron irradiation. The examples of materials development for advanced energy technologies demonstrate the trend away from the development of the materials themselves to consideration of material combinations and composites.

Keywords: materials development, power plant, fuel cells, nuclear fusion
THE ADVANCED TURBINE SYSTEMS PROGRAM IN THE U.S.A.

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Abstract
The Advanced Turbine Systems program was initiated by the U.S. Department of Energy, in cooperation with the gas turbine industry, to develop high-efficiency gas turbine systems for base-load utility and industrial markets. For electric utility application, the gas turbines will have an efficiency rating of at least 60 percent, improved environmental compliance and, in operation, will lead to a reduction in the cost of electricity. The efficiency goal for gas turbines intended for industrial power generation systems is defined differently: these will be at least 15 percent more efficient than current gas turbines for this service. The baseline fuel is natural gas. The program includes both the development of higher firing temperature capability and innovative cycles. In some designs, the efficiency goals mandate the use of turbine rotor inlet temperatures approaching those of current high-performance aircraft engines, together with a reduction in the amount of air taken from the compressor for use in cooling. As a result, the ATS program includes major initiatives in combustor design, airfoil design for improved aerodynamic efficiency, and more efficient schemes for cooling critical components. For industrial gas turbines, initiatives include the incorporation of cycle modifications such as recuperation and an advanced steam bottoming cycle, and the use of ceramic components. The materials needs for these developments are being addressed both by efforts specific to a given manufacturer, and by an overall support effort which is addressing (1) improvement of manufacturing processes for single crystal airfoils, (2) processing of thermal barrier coatings, (3) generation of mechanical property data for candidate ceramics, and (4) characterization of the modes of degradation of critical components (such as thermal barrier coatings) for use in improved life prediction modeling and in performance monitoring. The program involves the major U.S. gas turbine manufacturers, universities and National Laboratories. Demonstration of one advanced design for each area of application is expected by the year 2000.

Keywords: advanced gas turbines; single crystal alloy casting; thermal barrier coatings; properties of ceramics.
STEW PLANT MATERIAL DEVELOPMENTS IN JAPAN

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Abstract

Steam conditions for thermal power plants have recently been raised in order to respond to environmental protection and energy conservation concerns. In Japan steam conditions with a temperature of 600°C have already been adopted for newly constructed plants, and a 625°C class is expected to be realized soon; the final goal will be a 650°C class with ferritic steels. Since 1960 numerous studies on the heat resistant steels for boiler and turbine applications have been actively conducted. Among the various materials developed for advanced steam cycles, major progress has been seen in 9-12Cr steels for boiler pipe work and turbine components, and in austenitic steels for superheater and reheater tubings. In particular, recently developed ferritic 9-12Cr steels have become stronger than conventional austenitic stainless steels. Most recent 9-12Cr steels have a creep rupture strength of 140MPa at 600°C for 100,000 hours. Such enhancement in creep strength is achieved by the alloying of tungsten substituting molybdenum. Strengths of 180MPa at 600°C or 130MPa at 650°C are anticipated in the near future for ferritic steels by means of further studies on the role of alloying elements such as cobalt on creep strength. This paper deals with steam plant material developments and materials technology for advanced heat resistant steels in Japan.

Keywords: Boiler Material, Turbine Material, Heat Resistant Steels, Creep Strength, Hot Corrosion
THE NEW COST ACTION 522 - "POWER GENERATION IN THE 21ST CENTURY:- ULTRA EFFICIENT, LOW EMISSION PLANT"

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Abstract

The major challenge facing the power generation industry moving into the 21st century will be to achieve the targets of increased efficiencies brought about by stringent environmental regulations, whilst ensuring reliability, availability, maintainability and cost are not compromised.

Over the last decade the European COST programmes have made a considerable contribution in improving efficiency and reliability of power generation plant via major advances in materials technologies. Many of the materials and technologies developed in these programmes are currently in use in existing plant across the world.

Whilst significant benefits have been gained from the COST collaborations it was recognised that significant challenges still lay ahead. Therefore, during late 1996, the major European power plant manufacturers had discussions and brought together a new proposal which would address key technology areas to take the European power generation sector into the 21st century via continued collaboration. This proposal was approved by the EU in late 1997 and obtained the mandatory five signatures from participating countries government officials in April 1998.

This paper describes the objectives of the new COST action designated COST 522, gives an outline of the technical work packages that will be carried out and how the programme will be organised and administered.
Poster Presentations
A1 – A47
INVESTIGATIONS ON LARGE TURBINE CASINGS AND VALVE BODIES MADE OF NEW 9-10%CR-CAST STEELS AND IMPROVEMENT OF CASTING TECHNIQUE AND QUALITY PERFORMANCE

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Abstract
Steel castings made of creep resistant steels play a key role in fossil fuel fired power plants, for highly loaded components in the high- and intermediate- pressure sections of a turbine. Inner-, outer- and valve- casings, inlet pipes and elbows are examples for these critical components. In the development for higher efficiencies of the power plants and the improvement of creep resistance for the involved materials, also the casting steel grades have to be adapted to the increased demands on material properties. This paper shows the contribution of a steel foundry to the European COST-programme for the development of a new 10%Cr steel grade. It also shows the introduction of the new 9-10%Cr casting steels G-X 12 CrMoWVNbN 10 11 and G-X 12 CrMoVNbN 9 1 into commercial production of heavy castings.
CREEP PROPERTIES OF HEAVY WALL COMPONENTS FOR FORGED 9Cr-1.8W-0.5Mo-NbVN(NF616) STEEL.

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Abstract

W containing ferritic heat resistant steels, NF616, for boiler applications advanced especially in their creep resistance at elevated temperature. Increasing steam pressure and steam temperature for power generation plant accelerate the development of the latest W containing high creep rupture strength steels in order to apply the heavy wall components as main steam pipe and headers.

Forging process following the vacuum induction furnace or electric furnace melting produced the heavy wall NF616 components. Long normalizing time for homogenizing and tempering attained the tempered full martensitic micro-structure. Estimated creep rupture strength at 600°C and creep strain rate almost agreed those of thin wall NF616 steels in comparison.

According to the hardenability investigation through the continuous cooling rate transformation diagram, even 400mm thick wall pipe material indicates the homogeneous micro-structure. 3 hours normalizing is enough to obtain the uniform mechanical properties and stable creep properties.

Extracted residue amount change in elements tungsten, molybdenum, chromium and iron also well agreed those of the thin wall NF616 up to 10,000 hours aging. Therefore, long time creep properties are possibly follow the results of thin wall NF616 materials.

Keywords: Creep, Forging, Heavy wall, Ferritic steel, precipitation
LOW STRESS CREEP OF P91 TYPE HEAT RESISTANT STEEL

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Abstract

Short-term creep tests up to 3000 hrs were performed on a P-91 type heat-resistant steel at temperatures from 873 K to 923 K and stresses from 1 MPa to 95 MPa, using the helicoid spring specimens technique. The observed creep rates correspond to viscous behaviour under given conditions, in contrast to power-law creep behaviour at higher stresses. Since the stress exponent at higher stresses is 10 or more, the change in the deformation mechanism at lower stresses is proved.

The transition from viscous creep to power-law creep is relatively sharp and corresponds to independent contribution of the two mechanisms into total creep strain. The transition stress is about 100 MPa at 873 K and 65 MPa at 928 K. The service loading conditions of the steel correspond to the viscous creep area close to the transition to power-law creep. Extrapolation from power-law creep regime to low stresses can cause serious underestimation of predicted deformation rates.

The creep rates observed with P-91 steel under low stresses are lower than that of mild α-iron by less than three orders, while the difference under power-law creep regime is eight orders or more. Unlike under power-law creep regime, the creep-strengthening structural elements exhibit only low efficiency under viscous creep regime.

The creep rate at low stresses is in a very good agreement with Coble theory of diffusional creep. On the other hand, strongly pronounced primary part of creep curves cannot be simply explained by the diffusional creep theories. Since the grain size dependence of creep rate was not investigated in this work, it is impossible to identify operating creep mechanism reliably.

Though the effect of viscous creep mechanism on the creep rupture time remains questionable, it provides an alternative explanation for decrease of creep life in long-term experiments.

![Figure:Measured creep rates of P-91 steel at 873 K compared to creep rates of α-Fe and theoretical rates of Coble diffusional creep.](image)
Small Punch Tests on Steels for Steam Power Plant

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Abstract
Small punch test technique has been used to extract the mechanical properties of steam power plant components from using miniature specimens. Linear relationships were obtained between mechanical characteristics determined from small punch test and from standard tests. Analytical formulations were used to evaluate the uniaxial stress-strain mechanical behavior. Two approaches of the fracture mechanics have been applied to estimate the fracture toughness in the upper- and lower-shelf regimes. Estimated values of the fracture toughness from small punch tests were found to be comparable with those obtained from Charpy impact tests.

Keywords: small punch test, mechanical behavior, fracture appearance transition temperature, fracture toughness, modeling.
MACROSCOPIC CONSTITUTIVE LAWS FOR CREEP LIFE PREDICTION

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Abstract

Creep and creep fracture are phenomena of major practical relevance, often limiting the lives of components designed to operate for long periods under stress at elevated temperatures. For components and structures subject to creep loading, it is therefore necessary to know the stress which the relevant materials can sustain at the service temperatures without reaching some limiting creep strain and/or without creep fracture occurring within the planned design life. However, with modern power stations designed for lives over 30 years, procedures are required to allow the results obtained in short-term tests to be extrapolated to provide accurate long-term design data.

There are two factors which make such extrapolation difficult. First, there is no clear idea of the nature of the extrapolation functions which must be applied and this results in a requirement for long-term creep data with failure lives quite close to the design life. Secondly, even when suitable long-term data are available, they contain so much scatter that only order of magnitude estimates of creep life are possible.

During almost half a century of the research effort many different extrapolation methods have been proposed on different levels of sophistication. At present ideal life time prediction models do not exist but engineers still need to use prediction models which can be easily and reliably used to extrapolate short-term data to long lives with the minimum number of fit parameters that are required. At the same time, when using models it is important to be aware of their limitations as each existing model has different strengths and weaknesses.

Early work by Sandström and Kondyr reported a parametric procedure for long-term creep property extrapolation, termed the Ω method. Thus, the Ω methodology provides a challenging alternative to conventional theoretical and empirical approaches to creep life prediction. This alternative methodology has been very recently used by Nonaka et al. for evaluation of creep residual life for the modified 9Cr1Mo steel. The present paper has attempted to assess some of the limitations and the deficiencies of the Ω method by reference to the short-term creep tests (up to 15 000 hours) available for a high strength 9%Cr steel (Grade P91) at three temperatures from 823 to 923 K over a limited range of stress.
NOTCHED BEHAVIOUR OF P91 STEEL UNDER CREEP/FATIGUE LOADING

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Abstract
Smooth and circumferentially notched bars of P91 steel were tested under creep/high cycle fatigue conditions at 600°C in air. The strong notch strengthening effect due to stress triaxiality near the notch root was observed for pure creep and creep/fatigue loading with small cyclic stress component. Increasing cyclic stress component acts against the notch strengthening effect. Results of theoretical analysis of the stress triaxiality were correlated with the lifetime of notched specimens. Their lifetime can be predicted using the creep characteristics of smooth specimens; good agreement between experimental and predicted data was found.
CREEP CRACK GROWTH IN 9CrMoVNbN STEEL

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Abstract

A creep crack growth in the P91 type of steel made by VITKOVICE, a.s. is analysed. Tested material was both in an ‘initial’ and ‘aged’ state (after annealing at 625°C for 5000h) when the structural reactions resulted in a near - stable state, in which structure after long-term service exploitation was modelled. Experiments were carried out on DCBT specimens at temperature 600 °C and evaluated mathematically using adequate fracture mechanics parameters. Besides creep crack growth rates, also the time to initiation of creep crack growth were evaluated.

The main achievements are as follows:

1. formulation of the mathematical model of creep strain curves,
2. calculation of the redistribution of stress under creep and theoretical estimation of the time to crack initiation,
3. verification of the dependence of the time to crack initiation on the stress intensity factor,
4. verification of the dependence of the time to crack initiation on the fracture mechanics parameters.
RESEARCH AND DEVELOPMENT OF ADVANCED FERRITIC STEELS FOR 650 °C USC BOILERS

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Abstract
The creep rupture strength and oxidation resistance have been improved to develop advanced 9Cr steels for thick section boiler components of 650 °C ultra-supercritical (USC) plants. Thermo-calc calculation shows that the addition of high-Cr or high-Si for the improvement of oxidation resistance promotes the formation of δ-ferrite. Of the austenite stabilizing elements for suppressing the formation of δ-ferrite, high melting point elements Ir, Rh and Pd are promising for strengthening the martensite matrix because of their smaller diffusion rates and larger Young's modulus than those of Ni, Cu and Co. The creep rupture strength of 0.08C-9Cr-3.3W-VNBN steels increased with increasing Ir concentration up to 4%. The weight gain of 0.15C-8.5Cr-2W-VNBN steels during oxidation in air at 650 - 750 °C decreased with increasing Si concentration up to 1%. The combined addition of Si and Ti significantly improved the resistance to oxidation, indicating Ti can be used to substitute for a part of Si.
EFFECT OF Re ADDITION ON THE CREEP STRENGTH OF HEAT RESISTANT Cr-W STEELS

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Abstract

For the last several decades, extensive studies on heat resistant steels have been conducted to develop steam plant materials for boilers and turbines. The roles of alloying elements such as V, Nb, Mo, W, and Co are well recognized for the improvement of creep strength, and the amounts of these alloying elements have been optimized to obtain new grades of Cr-W heat resistant steels. With this background, in order to develop a method for the further improvement of creep strength, the effect of Re on the creep strength behavior of Cr-W steels has been studied; steels employed as base materials in this study include a 2.25Cr-1W steel and a 12Cr-2W steel. The addition of Re was found to remarkably enhance the creep strength of these Cr-W steels, particularly in a 2.25Cr-1.6W steel where the extrapolated creep rupture strength at 600°C for 100,000 hours was approximately 115MPa. This was due to the elevation of rupture strength in a higher value region of Larson-Miller parameter, which was stronger than Mod.9Cr-1Mo steel. This paper deals with the long term creep rupture properties and microstructures of Cr-W heat resistant steels containing Re.

Keywords: Rhenium (Re), Creep, Heat Resistant Steels, Cr-W Steels, Microstructures
Modelling of Low-Cycle Fatigue Behaviour of the Steel E911

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Abstract

The low-cycle fatigue (LCF) behaviour of the base material and of welds of the steel E 911 (X 10 CrMoWVNbN 9 1) with about 1 % tungsten has been determined for room temperature and for 600°C with and without hold times of 30 minutes. The data for room temperature lie at the upper bound of the scatterband of similar steels which has been determined earlier. The results for 600°C lie at the lower bound of the scatterband of similar results achieved for 550°C. Both cases show the good LCF-capability of this steel. For selected LCF conditions the hystereses were modelled by the use of constitutive equations based on the Robinson model. The model describes the behaviour at room temperature and at 600°C with and without hold times with two sets of parameters. The calculated and the experimental curves are in good agreement. LCF experiments with specimens with welds are tested at room temperature and at 600°C with and without holdtimes. These tests show a decrease in lifetimes by a factor of about two for the test types investigated here. The hold times decrease the lifetimes in addition.
THE MAIN PARAMETERS INFLUENCING THE CREEP RESISTANCE OF ADVANCED 9-12% CR - STEELS FOR POWER PLANT APPLICATIONS

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Abstract
A number of advanced ferritic-martensitic steels appeared in the last decade promising excellent creep behaviour compared to the materials used until now, 2 1/4 Cr 1 Mo and X20 CrMoV 12 1. The advanced 9 to 12 % Cr-steels show superior creep resistance in comparison with the reference material X20, which has been used very successfully over the past three decades. The creep resistance of the American development grade P/T 91 is surpassed by the W-containing grades P92 and E911. At present, further investigations on 9-12% Cr steels are in progress and numerous alloy compositions with various heat treatments are proposed. Creep data are obtained by extrapolation from short term tests. The experience shows that this method overestimates the creep rupture strengths of these materials and after the publishing of long term creep data the predictions often had to be revised.

Comprehensive microstructural investigations reveal that the as received microstructures of these materials underlies dramatically changes at service conditions, dependent from the temperature, alloy composition, heat treatment and applied stress/strain. Finally a thermodynamical equilibrium of the microstructure will be reached, which can be predicted very accurately with the aid of computers.

The microstructural stability is one of the most important factors for a good creep resistance of 9-12% Cr steels. A calculation model based on the determination of the transformation temperatures $A_{11}$ and $A_{12}$ is proposed, which can help to predict the microstructural stability from the chemical composition.

Keywords: ferritic chromium steels, microstructure, electron microscopy
EXPERIENCE IN THE MANUFACTURE OF STEAM TURBINE COMPONENTS IN ADVANCED 9-12% CHROMIUM STEELS

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Abstract
Recently, advanced 9-12%Cr ferritic steels have been developed suitable for use in steam turbines operating at temperatures up to 600°C. Two 412MW double reheat steam turbines have recently been built for Skaerbaek and Nordjylland power stations in Denmark. The advanced steam conditions of 285 bar/580°C/580°C/580°C necessitated the use of these new steels for high temperature rotor forgings, forgings for steam connections, bar and rolled rings for the construction of fabricated diaphragms and for major castings. The manufacture and processing of these components has demonstrated that large pieces in these materials can be produced with the required properties without significant problems, but that a high standard of technical control is required at all stages of the manufacturing process. This experience has provided a firm foundation for the future in which more highly alloyed steels of this family will be required as the inlet steam temperature and pressure are increased as a means of increasing the efficiency of large steam turbines.
OPTIMIZED CHEMICAL COMPOSITION OF 9–12 % Cr STEELS WITH RESPECT TO MAXIMUM CREEP RESISTANCE

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Abstract
Considerable effort has been devoted over several decades to improving the creep resistance of modified 9–12 % chromium steels. Possible ways were suggested consisting of increasing Mo and/or W contents, increasing nitrogen concentration, optimising V and Nb contents and adding boron. To avoid delta ferrite appearance in the microstructure, austenite forming elements such as nickel, cobalt and copper were added. The creep rupture strengths of these steels are reported to be double that of the well-known X 20 CrMoV steel. However, chromium modified steel is structurally very unstable. In the course of the creep exposure, secondary MX particles precipitate, which substantially strengthens the matrix. Precipitation of Laves phase accompanied by depleting matrix of Mo and W lowers solid solution strengthening. Z-phase (CrNbV nitride) and M2X precipitate after long time of creep exposure at the expense of MX and M2X. This does not substitute their precipitation strengthening effect. In order to optimize the chemical composition of modified chromium steels, all these processes have to be critically assessed with respect to the strengthening and degradation mechanisms.

Keywords: chromium modified steels, strengthening and degradation processes, optimized chemical composition, M23C6, MX, M2X, Laves phase, Z-phase, M6X
THE OPTIMIZATION OF HEAT TREATMENT FOR STEAM AND GAS TURBINE PARTS FROM 10.5 - 12 % Cr - STEELS.

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Abstract
There are considered optimization problems of heat treatment for steam and gas turbine blades, castings, disks and rotors from 10.5-12.0 % Cr -steel. Authors considered the problems of heat treatment for the large castings and welding joins from 10.5 % Cr - steels for optimization of creep fracture, creep ductility and creep crack resistance the base metal and welding joints. There is need to achieve the optimization of heat treatment for turbine castings, disks and rotors at the same time providing high mechanical properties in combination with stability of structure and long - term properties. Investigations on creep resistance and creep fracture had been carried out for 190,000h and over. The service properties can be improved through developed remelting processes (ESR, VEA) and heat treatment for base metal and welding joints.
NEWLY DEVELOPED 12% Cr HEAT RESISTANT STEELS FOR STEAM TURBINES

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Abstract
In order to improve the thermal efficiency for the effective consumption of fossil fuels and suppression of exhaust CO₂ gas, recently ultra super critical steam turbines with 593 to 610°C in main and/or reheat steam temperatures have been mainly constructed in Japan. Under such circumstances, the development of 12% Cr heat resistant steels for high temperature components remarkably contributes to the increase in steam temperature due to their excellent thermal stability.

As for high temperature rotors, three grades of 12% Cr steels (TOS101, TOS107 and TOS110) were developed, and are characterized by addition of Nb/Ta+N, 1% W and 1.8% W+Co+B to optimized 12CrMoV base alloy chemistry, respectively. TOS101 and TOS107 steel rotors have been successfully operated since 1973 and 1991, respectively. As well as rotor materials, heat resistant bucket materials and castings have also been developed. These materials are expected to enable the construction of fossil-fired units operated at 630°C or above.

Keywords: Steam turbine, 12% Cr heat resistant steel, Rotor, Bucket, Creep rupture strength
THERMAL-MECHANICAL FATIGUE BEHAVIOUR OF A 9 % CHROMIUM STEEL

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Abstract

Structural materials used in plants for power generation must have adequate resistance against creep, low-cycle thermally induced fatigue, high-cycle mechanically induced fatigue as well as against oxidation and corrosion. The group of 9 to 12 % chromium steels meets these demands at temperatures up to 550 °C. In comparison with austenitic steels or nickel-base superalloys, which allow higher temperatures, they have advantages concerning thermal conductivity, thermal expansion and economic aspects. In order to improve the efficiency of steam turbines, there are worldwide efforts to rise the operating temperature of these steels up to 600 °C. To achieve this, the experimental analysis and the assessment of the interactions between the microstructure and the deformation as well as the failure behaviour of these materials under thermal-mechanical loading is of utmost importance. Whereas there is a significant progress in the understanding of their creep behaviour which results from extensive research work, the consequences of start-ups, load changes and shut-downs are much less known. These processes result in thermally induced cyclic mechanical strains.

In this work, the thermal-mechanical fatigue (TMF) behaviour of a 9 % chromium steel (German grade X10CrMoVNb9-1) was investigated concerning the cyclic stress-strain response and the microstructural changes. TMF tests were performed with temperature being out-of-phase with the mechanical strain under total strain constraint with a minimum cycle temperature $T_{\text{min}} = 150$ °C and maximum cycle temperatures ranging from 450 to 650 °C. For some experiments dwell times between 3 and 20 minutes were introduced at $T_{\text{max}}$. Increasing $T_{\text{max}}$-values and dwell times reduce the number of cycles to failure. This is caused by the increase of the plastic strain amplitude, which is combined with increasing relaxation processes, and the development of tensile mean stresses. Simultaneously, the TMF induced softening of the microstructure becomes more and more pronounced. Cyclic softening is proved by the reduction of the amounts of maximum and minimum stresses as well as by the decrease of the microhardness measured after TMF. The subgrain structure is always changed during TMF. Higher $T_{\text{max}}$ lead to a spheroidizing and growth of the subgrains. A significant increase of the mean carbide size during TMF without dwell time is only observed at $T_{\text{max}} \geq 550$ °C. The growth of the carbides is rather dependent on the loading time than on the number of cycles. For the assessment of TMF life the Manson-Coffin relation, the Smith-Watson-Topper-parameter and the Ostergren-parameter are used. The TMF behaviour of the 9 % chromium steel is compared to that of a 12 % chromium steel.
THE DESIGN, MANUFACTURE AND INSTALLATION
OF A P92 HEADER

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Abstract

Because of crack damage detected during the routine inspection of a 2¼Cr1Mo header that had been in
service for 150 000 h at 560°C in the Kiel Power Station (GKK), a replacement header was required.
A new header was therefore designed using the 9% chromium steel P92 (Fe9Cr0.5Mo1.8WVNb),
based on the results of investigations carried out at the Research Centre Jülich in co-operation with
PreussElektro. The design calculations showed that the wall thickness of the new header pipes could
be reduced from the 44 mm necessary for 2¼Cr1Mo to 25 mm, reflecting the higher creep rupture
strengths of the 9% chromium steels. The design procedures are described and the new component is
compared with the old component. The manufacture of the 4 m long header pipes of 480 mm outer
diameter and 25 mm wall thickness is summarized with particular attention being given to the welding
procedures. The P92/P92 welds were carried out using a matching filler. The header nozzles were
manufactured from 2¼Cr1Mo and welded to the header using P91 filler metal. Quality control
especially of the on-site weldments is discussed and the installation of the new component in the
power station is described.

Keywords: 9Cr½MoWVNbN steels, P92, components, welding, quality control
EFFECT OF WELDING AND AGEING ON PROPERTIES OF NEW 9-12% STEELS

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New Cr-modified creep resistant martensitic steels were developed in the COST 501 project. They are being increasingly used as structural materials in power engineering structures. This is mainly due to their relatively high creep rupture strength, and toughness and good cyclic deformation behaviour in low cycle fatigue regime. These materials can be microstructurally unstable at high temperatures. The ageing, long time tempering and the welding has a great effect on the properties of these steels. Sometimes significant reductions in impact energy were observed with ageing and after welding.

Suitable welding parameters, preheating temperature and post weld heat treatments (PWHT) were planned and used. The welding process conditions used are summarized in Table.

This paper reports the changes in the behaviour of steels after long time 1000-10000 hours ageing at 600 and 650 °C temperatures and different welding processes of pipes: SAW for Ø 490 x 70 mm, SMAW for Ø 159 x 20 mm and GMAW for dissimilar welding.

Charpy impact values were measured at different temperatures after ageing and welding. Low cycle fatigue (L.C.F.) tests were carried out at RT and 600 °C. The Charpy transition curves will be given in Figures.

The absorbed energy of aged specimens tends to decrease continuously with ageing duration and temperature. The impact values of pipe materials after ageing at 600 °C up to 10000 hours are larger than 65 and 30 Joule at RT and -20 °C respectively. The toughness values of cast materials remained high enough after long term ageing too. The cycles to cracks of long term aged pipe material have decreased significantly while for the cast materials with B content increased between 0-6000 hours of ageing at 600 °C.

The impact energy in HAZ of SAW and SMAW welded material showed a high level some where higher than the base material. The impact toughness should be improved by higher PWHT temperature and using new filler materials.
MICROSTRUCTURE AND CREEP PROPERTIES OF P91 STEEL
AND WELDMENTS

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Abstract

The creep resistance of advanced chromium steels can be significantly increased due to precipitation of very small particles of vanadium nitride VN. The volume fraction of VN is controlled by N content which is available for formation of VN. The creep rate is then controlled by the mean interparticle spacing of M\textsubscript{23}C\textsubscript{6} and VN. In niobium bearing steels the effect of Nb(C,N) particles should be taken into account, too.

The strengthening of solid solution is caused primarily by the presence of Mo and/or W in solid solution. Precipitation of Laves phase occurring in the course of creep exposure decreases the molybdenum and/or tungsten content in the solid solution and thus lowers the solid solution strengthening. On the other hand, at the beginning of Laves phase precipitation small particles of Fe\textsubscript{2}(Mo,W) on subgrain boundaries contributes to the precipitation strengthening. Nevertheless, precipitation of Laves phase is finished after relatively short time. Coarsening of Fe\textsubscript{2}(Mo,W) that follows, as well as coarsening of M\textsubscript{23}C\textsubscript{6} and VN will act as one of the most effective degradation processes.

In order to obtain the material with advanced properties it is necessary to learn about all processes taking place in materials during long term exposure. Important is correct and rightful extrapolation of creep data, too.

Special attention has to be paid to the weld joints which usually represents the weakest point in any power equipment working in the creep regime. Creep resistance of weldments from modified chromium steel P91 was studied. Mechanical properties and results of creep-rupture tests of weldments were compared with those for the base material. Creep resistance of pipe and plate weldments is about 20-30% lower than that the base material.

Microhardness surveys were made in longitudinal sections taken through the central axis of the fractured cross weld specimens. The results of our investigations revealed that regardless of applied stress level the fractures occurred in the intercritical zone of HAZ which was a critical location of weldments.

Detailed microstructural investigations both base material and intercritical zone of HAZ were performed. In both regions an extensive precipitation of M\textsubscript{23}C\textsubscript{6} and secondary MX particles was observed. Some large primary NbX particles were also present in the microstructure. In long time creep test of weldments Laves phase particles were observed. No important differences in the type of minor phases was found between the base material and intercritical zone of HAZ.

Keywords: modified chromium steel, weldments, creep rupture strength, microstructure, microhardness profile
FATIGUE BEHAVIOUR ON MODIFIED 9Cr STEELS: BASE AND WELDS

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Abstract

The heavy wall piping used in headers and main steam lines of power generation plant is exposed to thermal fatigue damage during operating transients as well creep degradation during steady operation from the internal pressure and system loads. Experience show welded junctions to be the most critical parts on account of the reduced low cycle fatigue (LCF) and creep strength at such points. This can be attributed to factors such as:
- microstructural variation across the joint (parent - heat affected zone, HAZ - weld metal); some regions invariably possess inferior load sustaining capacity;
- corresponding variation in mechanical properties, leading to strain concentration at weaker points; this is the so-called metallurgical notch effect;
- for dissimilar metal welds thermal mis-match stresses and strains pose additional problems.

The results from low cycle fatigue tests on specimens machined from P91, P92 and E911 base (parent) materials are compared with those obtained for cross-weld specimens. These cross-weld results confirmed the widely reported criticality of the HAZ, indicating a mean cyclic life reduction factor of ≈ 2 to be necessary with respect to the base material.

Design life prediction normally relies on analysis of the stresses and strains in the weld section, calculated on the basis of the mechanical properties of the parent materials and neglecting those of the filler or the HAZ microstructure. The presence of the weld is accounted for by appropriate strength reduction factors on the creep and fatigue life curves. For LCF it is typical to apply a reduction factor of 2 on the cyclic life curve (ASME Code Case N-47) to account for the above-mentioned effects as well as uncertainties regarding the quality of the welding process itself [1].

For residual life estimation higher accuracy is needed and that means the following have to be considered:
- design baseline data are typically lower bound curves. For more accurate life prediction a material specific baseline curve is preferable, with the implication that, in eliminating this extra conservatism, experimental verification of the weld safety factors becomes more critical.
- There is little sense in applying advanced (and expensive) life prediction methods developed for the parent material if the results are in any case subject to large uncertainties via the simplistic application of conservative weld life reduction factors.
IMPROVEMENT OF CREEP RUPTURE STRENGTH OF 9Cr1MoNbV WELDED JOINTS BY NORMALIZING AND TEMPERING AFTER WELD

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Abstract
With the increase of steam parameters of coal fired thermal power plants, high strength 9%Cr steel containing niobium and vanadium became major material in boiler high temperature components. As the microstructure of these steels is tempered martensite, it is known that the softening occurs in HAZ of the weldment. In the creep rupture test of these welded joints the rupture strength is lower than that of the parent metal, and sometimes this reduction of strength is caused by Type IV cracking.

To develop an effective method to improve the rupture strength of welded joints, normalizing-tempering heat treatment after weld was proposed. 9Cr1MoNbV plates with thickness of 40-50mm were welded by narrow gap MAG welding procedure using modified welding material. After normalizing at 1050°C and tempering at 780°C, strength properties of the welded joints were examined. Microstructure of HAZ was improved as before weld, and rupture strength of the welded joints were equal to that of the parent metal.

Keywords: Heat resistant ferritic steel, Welding, HAZ, Creep, Type IV cracking
CHARACTERISATION OF THE WELDABILITY AND
BEHAVIOUR OF THE HEAT AFFECTED ZONE
FOR STEEL E911

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Abstract
The aim of this study was to determine the influence of varying heat inputs on the
weldability and the behaviour of the heat affected zone (HAZ) of steel E911. Basic
investigations on the weldability were performed on pipe joints manufactured by shielded
metal arc welding (SMAW) and submerged arc welding (SAW). Gleeble simulations
representing thermocycles like in actual SMAW and SAW were applied to produce
simulated HAZ microstructures. After post-weld heat treatment (PWHT) pipe joints and
simulated specimens were subjected to hardness tests, metallographic investigations,
constant strain rate tests, and creep tests. Particular attention was given to the softening
effect in the HAZ and its influence on the creep resistance of the welded joint. Results from
pipe joints show the decrease of creep resistance values of the tungsten modified version
E911 to be less pronounced than observed for standard P91.

Keywords: weldability, steel E911, mechanical properties, creep properties
DEVELOPMENT OF 12%Cr HEAT RESISTANT STEEL PLATE (TEMPALOY F-12M) FOR USC BOILER

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Kawasaki, Japan

Abstract
This paper deals with newly developed 12%Cr ferritic heat resistant steel plate (TEMPALOY F-12M) containing 0.7Mo-1W-0.1Mn-B-Cu-Nb-V-N which is used for hot reheat steam pipes and headers with large diameter and thick wall of USC boiler. The steel has high steam oxidation resistance, and creep rupture strength of more than 1.3 times higher as compared with Mod.9Cr-1Mo steel (ASTM A387 Gr.91) above 600 °C, which is attributed to strengthening by lower Mn and B addition as well as precipitation strengthening of Nb, V carbonitride and W strengthening. In addition, the steel plate consisting of fully tempered martensitic structure exhibits enough notch toughness after not only PWHT but also a long term aging, and good hot and cold workability and weldability.

Keywords: ferritic steel plate, creep rupture strength, steam oxidation resistance
CREEP RUPTURE STRENGTH AND STRENGTH REDUCTION FACTOR OF WELD JOINTS IN BOILER TUBES OF TYPE 2.25Cr-1Mo STEEL

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ABSTRACT

The work deals with the evaluation of long-term creep rupture strength and strength reduction factor (SRF) of two welded joints both SMAW and automated orbital GTAW welds in boiler tubes of type 2.25Cr-1Mo creep resistant steel.

The dominant weakest locality controlling creep rupture strength of both these welds is heat affected zone. That is why a loss of weldment rupture strength is expected in comparison with base metal used. To quantify this decline, the SFR parameter is calculated as the ratio between rupture strength of weld joint and material of boiler tube used at constant temperature and time to rupture. This conception of SRF enables to express the real influence of welding technology on long-term creep rupture strength of material investigated.

The results obtained reveal that

- at the shortest times to rupture in the temperature region 550 to 600°C, SRF values are time independent and equal to 1
- at longer times to rupture, the SRF declines evidently with increasing time to rupture
- the beginning of declining branch of SRF time dependence shifts to shorter time with increasing temperature
- the calculated SRF value are in relatively good agreement with those parameters recommended acc. to ASME Code, Case N-47-32.
DEVELOPMENT OF 2Cr-Mo-W-Ti-V-B FERRITIC STEEL FOR ULTRA SUPER CRITICAL BOILERS
(NKK TEMPALOY F-2W)

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Abstract
This paper deals with newly developed 2Cr-Mo-W-Ti-V-B ferritic heat resistant steel tube (TEMPALOY F-2W) which is used for water wall tubes and the economizer tubes of USC boilers, and for superheater tubes and reheater tubes of SC boilers. This steel is made by adding Mo and W as solution strengthening elements, and V and Ti as precipitation strengthening elements to a base of 2% Cr steel in order to improve its high temperature strength, and one whose matrix is a bainite single phase. The developed steel has superior creep rupture strength, its ordinary temperature and high temperature strengths are almost 1.5 times those of 2.25Cr-1Mo, and its allowable stress is equal to that of 9% Cr high strength material, SA213-T91(9Cr-1Mo-Nb-V). Cost advantages can also be expected by reducing the wall thickness of tubing in boiler design due to its high strength. This newly developed steel is a material usable as for water wall tubes up to the 575°C range in future high temperature, high pressure plants.

Keywords: ferritic steel, bainite phase, solution strengthening, precipitation strengthening
PROPERTIES AND EXPERIENCES OF A NEW AUSTENITIC STAINLESS STEEL SUPER304H (0.1C-18Cr-9Ni-3Cu-Nb-N) FOR BOILER TUBE APPLICATION

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Abstract
A new economical austenitic stainless steel (SUPER304H: 0.1C-18Cr-9Ni-3Cu-Nb-N) with high elevated temperature strength has been developed in Japan for boiler tube application. The allowable tensile stress of this stainless steel is more than 20% higher compared with that of ASME SA-213 Grade TP347H. This excellent creep rupture strength is based on the precipitation strengthening effect of fine Cu-rich phase which precipitates coherently in the austenitic matrix during service-exposure. The corrosion resistance of this stainless steel is almost the same as that of fine-grained TP347H. The SUPER304H tubes have been service-exposed as superheater tubes and reheater tubes, and the 6.5 years service-exposed tubes confirmed that this new stainless steel was applicable as boiler material. The SUPER304H tubes have already been approved by MITI standard in Japan and have widely been used as superheater tubes in Japanese fossil fired boilers.

Keywords: austenitic stainless steel, boiler tubes, superheater tubes, high-temperature applications, seamless tubes
PROPERTIES AND EXPERIENCES FOR ALL PRODUCT FORMS
OF GRADE 23 (HCM2S) STEEL
FOR FOSSIL POWER GENERATION

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Sumitomo Metal Industries (Japan)

Paper will be distributed at the meeting.
PROPERTIES AND EXPERIENCES FOR ALL PRODUCT FORMS OF GRADE 122 (HCM12A) STEEL FOR FOSSIL POWER GENERATION

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Paper will be distributed at the meeting.
Steam-side oxidation of ferritic steels

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Abstract
The oxidation susceptibility of ferritic steels in superheated steam has been evaluated in the temperature range 500 to 750 °C. The results indicated that the alloy HCM2S had the same oxidation behavior as T-22 and that no advantage existed in using 9 and 12 % Cr alloys like E-911, NF616 and HCM12A between 600 and 650 °C. The alloy St12T (X20) gave superior oxidation resistance with T-91 being second best but susceptible to spallation upon thermal cycling.
The oxidation mechanism requires the transport of water molecules through an outward growing magnetite layer controlled by the diffusion of Fe-cations through the inner oxidation front. Attempts to modify the oxidation kinetics should be aimed at modifying the structure of the outer magnetite layer. Preliminary results with alloy HCM2S at 600 °C suggest that additions of boric acid to the steam could modify the environment at the alloy surface to promote the formation of more protective oxides.

Keywords: Steam oxidation, T-22, HCM2S, T-91, E911, NF616, HCM12A
Steam oxidation properties of high Cr ferritic steels

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Abstract
This paper discusses the effect of Temperature and Cr content on the steam oxidation behavior of high Cr ferritic steels used for Ultra super critical boiler. Steam oxidation tests were conducted in 550 - 750°C steam of atmospheric pressure for up to 2,000 hours. It was found that parabolic oxidation kinetics adequately described the steam oxidation process for all tested alloys and the parabolic rate constant $K_P$ decreases with increasing Cr above 650°C. The observed $K_P$ value agrees with the estimated $K_P$ value which is calculated by regression equations related with Cr and Si contents for all tested alloys. By metallurgical examination, Low oxidation rate of high Cr ferritic steels are based on the continuous Cr-rich layer observed in the inner oxide scale at the metal/oxide interface.

Keywords: ferritic steel, steam oxidation, superheater tube, boiler, kinetic
A New Titanium Nitride Dispersion Strengthened Ferritic Steel for High Temperature Applications

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Abstract

Conventional 9-12% Cr steels used in modern plant designs are ultimately limited in their long term creep performance by the stability of the carbides and carbo-nitrides which precipitate in the steel during tempering and subsequently during service. The present work aims to develop a new type of ferritic steel which contains a fine dispersion of highly stable titanium nitride particles to confer long term microstructural stability and high temperature strength to the steel. The key to the production of this new material is to reactively process the titanium containing steel with a solid state nitrogen donor powder (chromium nitride) using either powder metallurgy or spray forming technology.

This paper presents the powder metallurgy and spray forming procedures developed to achieve the fine dispersion. Creep tests in the temperature range 600-700°C were performed at each stage of the alloy development. Initial evaluation revealed that the creep properties were limited by the fine grained structure of the material, which resulted from the development of a stable particle dispersion. Thermo-mechanical treatments have been successfully developed to produce creep resistant grain structures similar to Mechanically Alloyed Oxide Dispersion Strengthened (MA-ODS) alloys. Transmission electron microscopy observations have shown that particle size, particle spacing and volume fraction of titanium nitride in the prototype alloys are in accordance with the Hertz model. This model has been utilised in the optimisation of the alloys and the subsequent improvement in creep properties is discussed in relation to the interparticle spacings and dislocation particle interactions.
DEVELOPMENT OF A NEW HEAT RESISTANT AUSTENITIC STAINLESS STEEL FOR HIGH TEMPERATURE COMPONENTS OF POWER GENERATION

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Abstract

New austenitic stainless steel, NAR-AH-4, which consists of LowSi-23Cr-11.5Ni-0.2N-B-REM has been developed for the application of high temperature components (up to 1000°C) in the thermal power plants and chemical plants. The corrosion and erosion resistance for developed steel with high content of chromium and slight amount of REM is excellent by forming adherent chromia oxide film on a surface. The creep rupture strength is considerable higher than that of Type 310S(25Cr-20Ni) and Alloy 800H(20Cr-32Ni-Al,Ti) due to the addition of nitrogen and boron. The resistance to weld hot cracking sensitivity for this steel is better than that for Type 310S and high silicon content austenitic stainless steels, due to decreasing silicon content (0.3%) and optimum ratio of chromium equivalent to nickel equivalent. In addition, this steel has an economic advantage over Type 310S as well as Alloy 800H.

These results indicate that this steel is expected to be widely utilized as candidate materials for high temperature components.

CORROSION PROTECTION OF AISI 304 AUSTENITIC STEEL BY Y AND Er ION IMPLANTATION AGAINST ISOTHERMAL OXIDATION.

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Abstract.
The beneficial effects of the addition of yttrium and erbium by ion implantation on the oxidation behaviour of an AISI 304 stainless steel at 1173 K have been investigated. Isothermal oxidation experiments have been established up to 500 h of test. The effect of the so-called reactive elements (REs) has been studied before in order to enhance the oxidation behaviour of different alloys. In this work the effect of Er as a RE candidate has been analyzed in compared to another RE used before such as Y. The results show that yttrium and erbium have both the same effect, reducing significantly the corrosion rate and improving the adhesion of oxide scale. Theoretical calculations have been performed in order to achieve the best depth profile thus identifying the surface damage during the implantation process.
NEW 2-3%CR STEEL GRADES FOR WATERWALL PANELS AND SUPERHEATERS

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Abstract

The positive effects of Tungsten and microalloying elements (V, Nb and B) on high temperature properties of steel grades in power generation applications are already widely used in Chrome-Molybdenum steels containing between 9 and 12% of Chrome (T91/P91, T92/P92, E911, ...).

More recently, the same additives have been used in lower alloy steel grades, such as those containing 2-3% of Chrome, thus producing the future ASTM A213 grade T23 (also described by ASME in Code Case 2199) and grade 7CrMoVTiB 10-10. Vallourec and Mannesmann Tubes have been involved for several years in developing these new steel grades, and the results of experiments have revealed the following two advantages:

- excellent mechanical properties at high temperatures, which are much better than those of grades T22/P22.
- improved weldability due to the low Carbon content (making post-welding heat treatment unnecessary).
DESCRIPTION OF THE PRECIPITATION BEHAVIOUR OF ADVANCED 9-12% CR STEELS FOR POWER PLANT APPLICATIONS

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Abstract
Mainly for temperatures above 560°C there is a great demand to replace the widely used austenitic tube materials through advanced ferritic-martensitic steels, in order to utilise their better thermal conductivity, lower thermal expansion coefficient, lower costs and better resistance against stress corrosion cracking susceptibility.

The knowledge about the state of precipitates, which is dependent from temperature, time and stress/strain, is significant for the prediction of the creep properties of these steel grades. To overcome the problem of fulfilling the demand of designers, to offer reliable long term creep properties for newly developed steels in short amount of time and additionally lower the risk of producing non-reliable figures as well as a guide for the development of a promising alloy concept, the modelling of the microstructure based on thermodynamic calculations is used. The results are phase diagrams showing the precipitates to be expected as well as driving forces, phase compositions and diffusion coefficients. Different steel grades can be evaluated by comparing these data.

Keywords: modelling, creep, precipitation, ferritic chromium steels, thermodynamics
HIGH RESOLUTION MICROANALYSIS OF CHROMIUM STEELS P92 AND P122

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Abstract
Extensive alloy development of 9-12% chromium steels for high temperature use has taken place over the last decade and two of the most promising materials available today are NF616 and HCM12A, now ASME code approved as P92 and P122. In order to understand the role of different alloying elements, a combination of atom probe field ion microscopy (APFIM) and analytical transmission electron microscopy (ATEM) has been used in this work to obtain a detailed knowledge of the microstructure and the distribution of elements. The investigation concerns the microstructural evolution of the two steels P92 and P122 during isothermal ageing at 600°C for up to 10000 h. The composition of the investigated materials is given in Table 1. The main difference between the two steels, as can be seen in Table 1, is an addition of copper to P122 with the intention to suppress δ-ferrite formation and allow a higher chromium content. APFIM has been used for chemical analysis of the different phases present. Precipitates of type M23C6, MX and Laves phase as well as the matrix have been analysed in the two materials at different times of ageing.

Table 1. Composition of investigated materials (wt%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Mo</th>
<th>W</th>
<th>Si</th>
<th>P</th>
<th>V</th>
<th>Nb</th>
<th>N</th>
<th>B</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>P92</td>
<td>0.11</td>
<td>8.96</td>
<td>0.46</td>
<td>0.06</td>
<td>0.47</td>
<td>1.84</td>
<td>0.04</td>
<td>0.008</td>
<td>0.20</td>
<td>0.07</td>
<td>0.05</td>
<td>0.001</td>
<td>-----</td>
</tr>
<tr>
<td>P122</td>
<td>0.11</td>
<td>11.0</td>
<td>0.56</td>
<td>0.32</td>
<td>0.42</td>
<td>1.94</td>
<td>0.02</td>
<td>0.013</td>
<td>0.19</td>
<td>0.05</td>
<td>0.05</td>
<td>0.001</td>
<td>0.87</td>
</tr>
</tbody>
</table>

It was shown that the matrix concentration of copper in P122 drops during ageing to an equilibrium level at about 0.1% (by weight). No copper was found in M23C6, MX or Laves phase. The copper instead forms a separate phase. This phase was not analysed with APFIM, but instead ATEM was used to confirm its existence. Small amounts of boron added to 9-12% chromium steels have been found to give a positive effect on long term creep resistance, but the reason for this is not yet fully understood. This investigation showed that most of the boron exists in M23C6 carbides, possibly affecting the properties of this phase. During ageing the amount of tungsten in the matrix drops due to formation of Laves phase. This process is faster in steel P122 compared to steel P92, indicating an accelerating effect of copper on the nucleation of Laves phase.

Keywords: 9-12% chromium steels, atom probe field ion microscopy, TEM, boron
EFFECT OF MICROSTRUCTURAL EVOLUTION OF A T91 STEEL DURING CREEP

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The creep response of a 9Cr-1Mo-NbV steel was investigated at temperatures ranging from 575 to 650°C. The minimum creep-rate dependence on applied stress was well described by means of a conventional power law, the stress exponent increasing when temperature decreased. Detailed microstructural analysis was carried out by Transmission Electron Microscopy on samples tested at 575 and 600°C until rupture or after interruption of the test. In the as received condition, the microstructure of the steel consisted of elongated subgrains whose boundaries were decorated by relatively large particles (M23C6 and primary undissolved MX). After creep exposure, subgrain growth was accompanied by a reduction in free dislocation density, while an additional precipitation of very fine particles (MX) occurred early in the tests; as a result, all creep samples showed a bimodal population of precipitates, both subject to coarsening during creep. The coarsening process was described by means of the Ostwald ripening law; in particular, the coarsening process for both large (mainly M23C6 particles) and fine (MX) precipitates was found to depend on stress. A simple empirical relationship was then used to relate the coarsening constant with applied stress.

The strengthening effect due to both large and fine precipitates was analysed in terms of threshold stresses; in particular, each family of precipitates was assumed to produce a threshold stress whose magnitude was proportional to the Orowan stress. The effective threshold stress was then calculated as the sum of the individual threshold stresses generated by the different families of precipitates. The resulting constitutive equation was used to describe the minimum creep-rate dependence on applied stress for the investigated 9Cr-1Mo-NbV; the comparison between calculated curves and experimental points at 575 and 600°C was satisfactory. Then, the same model, with different values of the microstructural parameters (initial size of the precipitates and appropriate values of the coarsening constant and of the volume fraction of the secondary phases) was used to describe the minimum creep-rate dependence on stress for 9Cr-1Mo and 9Cr steels. The agreement between calculated curve and experimental points for the 9Cr-1Mo steel was fairly good, especially in the low stress regime. By contrast, in the case of the 9Cr steel, the model underestimated the minimum creep rate at a given stress even though the value of the stress-sensitivity parameter was substantially correct. This discrepancy was attributed to the effect of solid-solution strengthening elements (Mo or W) on the temperature-dependent parameter \( A' \), an effect previously observed in FCC metals. In this context, the model could be used as a basis for achieving a correct interpretation of the creep behaviour of the new W-bearing steels (9Cr-1Mo-NbVW).
QUANTITATIVE EVALUATION OF PRECIPITATES IN THE MARTENSITIC CAST STEEL G-X12CrMoWVNbN10-1-1

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Abstract
In this paper a procedure for the investigation of precipitates appearing in 9-12%Cr-steels is introduced. The study was performed on a series of creep rupture specimens of the cast material G-X12CrMoWVNbN10-1-1 crept at 600°C up to 33410h. By means of the energy filtering electron microscopy method (EFTEM) a size estimation of M23C6 carbides, MX phase, Laves Phase and Z-phase is given for the as received condition as well as the long term crept condition. The growth and coarsening behaviour of the investigated precipitates are discussed.

Keywords: electron microscopy, EFTEM, microstructure, ferritic chromium steels
MICROSTRUCTURAL INVESTIGATIONS OF 9%CR STEEL P92 AFTER LONG-TERM CREEP DEFORMATION

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Abstract

The microstructure and creep properties of the 9Cr-0.5Mo-1.8W-V-Nb steel P92, a Japanese steel developed for advanced coal-fired power stations with operating steam temperatures around 600°C, have been investigated. The objective was to examine quantitatively the changes in the microstructure which occur during long-time exposure (up to around 33000h) at service temperatures and to evaluate the relationship between microstructure and creep rupture behaviour. Using analytical transmission electron microscopy of thin foils and extraction double-replicas, statistical quantitative analyses of the P92 microstructure were undertaken to determine the dislocation density within the subgrain, the width of the martensite laths/subgrains and the particle size distribution in the as-received condition and after creep testing at 600 and 650°C. The study showed that the microstructural changes responsible for the decreasing creep rupture strength were a marked decrease in dislocation density and continuing polygonization of the dislocation structure, together with coarsening of the M23C6 precipitates. The M(C,N) precipitates were found to be resistant to significant coarsening during creep exposure. The precipitation of the Laves phase Fe3(W,Mo) and its effect on the long term creep strength is discussed.

Keywords: 9Cr1MoVW6NbN steel, P92, carbide precipitation, Laves phase, dislocation density
MICROSTRUCTURAL EVOLUTION DURING CREEP OF THE NEW MODIFIED 9% CR-STEEL WITH BORON AND COBALT

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Abstract

The new modified 9% Cr steel with boron and cobalt is a further development of the ferritic 9-12% Cr steels for the use in low emission coal fired power stations. Continuous and interrupted creep tests were performed under different initial stress levels at 600°C and 650°C. Creep behaviour of the new steel is shown by means of different plots of the creep parameters. The results of the creep tests show significantly lower creep rates for the referred new 9% Cr steel in comparison with conventional steels which promises longer life time of the components. The quantitative and qualitative characterisation of the microstructure was carried out after defined steps of creep deformation and different periods of ageing. Special emphasis is paid to the development of the dislocation structure and precipitation processes. The microstructural results are correlated with the creep behaviour of the material. The microstructural features responsible for the higher creep resistance are shown and discussed. In particular the affect of M23C6 precipitates on the microstructural stability and hence on the higher creep resistance of the referred steel are stressed out.
Dislocation Substructure Degradation during Creep of Martensitic Heat-resisting Steels with and without W

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Abstract
Recovery of martensitic lath structure was studied in creep of 11Cr-3W steel and Mod.9Cr-1Mo steel, to elucidate the role of W in the improvement of creep strength. Creep deformation induces recovery of martensitic lath structure. Dislocation networks forming lath boundaries are unknitted, and lath width increases with increasing creep strain. The lath width finally saturates to a value determined by applied stress. The saturated values of the two steels are the same under the same creep condition. However, growth rate of lath width is slower in the W containing steel. The slower growth of lath width results in the lower creep rate and the consequent longer rupture life of the W containing steel. Residual life assessment of the steels is discussed on the basis of the evolution of lath structure.
Microstructural investigation of advanced creep resistan
10%Cr steel

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Abstract
Steels operating in creep regime in power plant components may undergo during service
a microstructural evolution that can affect their mechanical properties. The present work
deals with microstructural analysis of the creep-tested samples of the forged 10 % Cr steel.
Quantitative data of the dispersion and chemical analysis of the phases present and of the
evolution of the dislocation structure have been measured. Microstructural features have been
correlated with creep strength. The results have been obtained within the
COST 501/III/WP11 project.

Keywords: martensitic steels, microstructure, creep, electron microscopy
Microstructural Stability During Creep of Mo-and/or W-bearing 12Cr Steels

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Abstract
The evolution and stability of particulate phases during creep of molybdenum or tungsten-bearing 12Cr steels have been investigated in considerable depth. The important finding is that the kinetics of Laves phase precipitation in the molybdenum-bearing alloy are significantly different from those in the tungsten-bearing alloy. It is generally believed that such differences in kinetics will influence creep behaviour. Data on Laves phase precipitation kinetics as a function of time and temperature were quantified using the Wert-Zener equation in conjunction with the proprietary software Thermocalc to determine equilibrium solute concentrations in these complex steels. The progressive depletion of Mo and W from the matrix as the particles of Laves phase evolve has been quantitatively modelled using experimental data obtained on both steels over a range of time and temperature. Isothermal coarsening rates of M₂₃C₆ and MX carbide particles were measured and found to occur at constant volume fraction in accordance with Ostwald ripening kinetics, with no significant differences in rates found between the two steels. The coarsening rates of M₂₃C₆ particles, found on subgrain boundaries, were consistent with a third power dependence on particle radius with an activation energy similar to that of volume diffusion. The smaller MX particles, which lay on subgrain-interior dislocation lines, were better explained by dislocation pipe diffusion with a fifth power dependence on particle radius and an activation energy approximately half that of volume diffusion.

Keywords: 12Cr steels, creep, phase stability, kinetics, Thermocalc
MICROSTRUCTURAL DEGRADATION OF MARTENSITIC
12%Cr POWER PLANT STEELS DURING PROLONGED HIGH
TEMPERATURE CREEP EXPOSURE

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Abstract

Detailed microstructural studies have been carried out on a series of tempered martensitic
12CrMoVNb steels which exhibited sigmoidal creep rupture behaviour when tested at
temperatures of 550°C and above out to durations beyond 100,000 hours. This behaviour has
been shown to be associated with marked softening of the materials due to microstructural
degradation effects occurring during the creep process. Electron microscopy studies have shown
that these effects take the form of dissolution of the fine M2X and MX matrix precipitates as
well as precipitation of coarse particles of M2X, Z and Laves phases. In addition, progressive
coarsening of the M23C6 carbides at prior austenite and martensite interlath boundaries occurred
together with the formation of extensive sub-grain networks. These processes result in the creep
rupture strength of the steels progressively changing during creep exposure from being initially
controlled by precipitation strengthening to being dependent in the long term on solid solution
hardening, thus accounting for the observed sigmoidal inflexion in their high temperature creep
rupture characteristics.
MICROSTRUCTURAL PHYSICALLY BASED CREEP MODELLING

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Abstract
The relation of the microstructure and macroscopic creep behaviour of a steel is a well known and investigated fact. Commonly, creep-models use this in form of the plasticity-concept of Bailey-Orowan to couple the microstructure to plasticity. The various existing models do not contain the description of the microstructure in a self-consisting, physical way. In this contribution it is shown that by means of physical modeling, the kinetic of the dislocation-microstructure can be described and more quantitatively understood for a simple material. By the generally kind of the dislocation-model, it is possible to verify it by different simulation types like recovery, relaxation and creep which are strongly related. The introduced basic model is thereby verified and can be used with further extensions for more complex steels. A treated question is the influence of distributed microstructural parameters e.g. the subgrainsize-distribution. Therefore a simulation study is presented.

Keywords: dislocation model, microstructure, creep, recovery
THE SURFACE STRUCTURE OF GAS TURBINE BLADES

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Abstract

The X-ray analysis method has been used to study the phase structure of gas turbine blades in operation. The structure and composition of oxide, sulfide and sulfate phases as well as the structure of oxides on electron-beam MCrAlY coated surfaces have been established for fixed and rotor nickel-base alloy blades after service. The phase state of matrix solid solution of the coating in different blade areas after service has been investigated.

Keywords: gas turbine blade, surface, operation, X-ray diffraction method, phase structure
LONG-TERM CREEP AND CREEP RUPTURE PROPERTIES
AND MICROSTRUCTURAL CHANGES
OF HEAT RESISTANT STEELS

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Abstract
The NRIM (National Research Institute for Metals) Creep Data Sheet Project which aiming
to produce long-term experimental creep and creep rupture data such as 100,000h creep
rupture strength on 47 kinds of commercial engineering creep resistant steels and alloys, has
been continued since 1966. The present status of the Project and the recent research
activities on long-term creep and creep rupture properties are described. The long-term
creep and creep rupture properties, microstructural evolution and its effect on creep strength
property and creep crack growth behaviour have been investigated for the creep resistant
steels. The behaviour has been shown to be complicated at long times, reflecting
complicated microstructural evolution during creep.
Microstructure control of martensitic phase matrix in advanced ferritic steels for USC boilers to achieve long term stability

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Abstract
Effects of alloying elements on the relevant phase equilibria, and thermodynamic stabilization and strengthening of martensitic phase matrix of the steels in question have been studied to establish the fundamental guiding principles to achieve new ferritic steels with improved creep strength used for 650 °C ultra super critical (USC) boilers. The final phase equilibria to be considered for the microstructure of the steels in question has been found to be $\alpha$, $MX$, $M_2\text{C}_6$ and Laves phases. The roles of each alloying element on thermodynamic stabilization and strengthening of martensitic phase matrix have been clarified by evaluating $T_s$ temperature and compiling $M_s$ temperature data. Some of the ferrite-stabilizing elements such as Mo and W are found to be effective both to increase thermodynamic stability and strengthening of the martensite. The austenite-stabilizing elements such as Re, Ir, Rh, Pt and Pd have been found to be very effective to strengthen the martensitic phase matrix compared with the conventional elements such as Cu, Ni and Co, although they reduce thermodynamic stability of martensite at high temperatures. Effect of Ir addition on microstructural change and creep-related properties has experimentally been examined for model steels with a base composition of 0.08C-0.3Si-0.5Mn-Fe-9Cr-3.3W-0.2V-0.05Nb-0.05N. The addition of Ir to the steels is found to increase resistance to softening of martensite at high temperatures and to be one possibility to increase long-term creep rupture strength of the steels at elevated temperatures over 600 °C.

Keywords: USC boilers, advanced ferritic steels, creep strength, martensite
PROPERTIES AND MICROSTRUCTURE OF MODIFIED 9CR STEELS

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Abstract

The steel Grade E911 has been developed from Grade P91, in the frame of the European 501 COST Programme, to increase the creep properties at 600°C through the control of vanadium, nitrogen and the addition of tungsten. The comparison between Grade P91 and E911 in terms of mechanical and creep properties, long time exposure, both in term of mechanical and microstructure evolution, are presented. The Grade 911 shows a performance better than Grade 91: its extrapolated stress to obtain a rupture at 600°C in 10⁸ hours is now about 110 MPa instead of 95 MPa for the Grade 91. Microstructure stability of both the steels was investigated by isothermal ageing tests for up to 10000 hours at 600 and 650°C and some mechanical behaviour are compared. The results show that the tensile properties and ductility are maintained.

KEYWORDS: high chromium ferritic steel, creep, microstructure evolution, COST programme, P91, E911.
Poster Presentations
B1 – B15
CORROSION BEHAVIOUR OF SOME STEELS AND ALLOYS IN COAL GAS ENVIRONMENT

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Abstract
Ten types of low and high-alloy steels were subjected to the isothermal and cycled long-term corrosion tests in the coal gasification environment. Test temperatures were 500, 700 and 900°C. The best results were obtained for AISI 310, INCOLOY 800 H and ODM 751 steels. It turned out, that the cycled test models operating conditions better than the isothermal one.

Key words: heat resistant materials, high temperature corrosion, coal gasifier environment
LABORATORY INVESTIGATION OF HIGH TEMPERATURE CORROSION IN STRAW-FIRED POWER PLANTS

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Abstract
Corrosion in straw fired power plants has been studied in the laboratory for Sandvik 8LR30 (18Cr 10Ni Ti) and Sanicro 28 (27Cr 31Ni 4Mo). The influence of HCl and SO₂ was investigated at 600°C metal temperature for up to 300 hours. In addition the corrosion behaviour of the same materials was examined after having been exposed under a cover of ash in air at furnace temperatures from 525 - 700°C. The ash was either actual ash taken from a superheater in a straw-fired boiler or synthetic ash consisting of components found in real ash (KCl and K₂SO₄). Exposures were undertaken combining the aforementioned aggressive gas environment with the ash deposits. Thus the corrosion potential of individual components (namely HCl, SO₂, KCl and K₂SO₄) were evaluated. Experiments were also conducted where the metal temperature was 600°C whilst the flue gas temperature was 800°C to simulate the temperature difference encountered in superheaters.

Keywords: high temperature corrosion, ash deposits, gaseous corrosion,
INFLUENCE OF SULPHIDIZING-OXIDIZING ENVIRONMENT ON CREEP BEHAVIOUR OF SOME HIGH TEMPERATURE MATERIALS

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ABSTRACT

Coal gasification and utilisation of combined cycle represents an environmentally as well as economically advantageous process of energy conversion in power plants. The main constituents of coal gas are CO, CO₂, H₂, H₂O, CH₄ and sulphur compounds, mainly H₂S. This multicomponent medium constitutes a very aggressive atmospheric condition and corrosion degradation represents the main life-limiting factor of metallic parts in gas path (for example in raw gas heat exchangers). Corrosion aggressivity of this medium is growing with an increase in temperature, pressure and concentration of harmless constituents. A general demand of designers is to use still higher parameters for the conversion process. Temperatures of about 500°C seem to be acceptable from the corrosion point of view when high corrosion resistant materials are applied. Apart from corrosion it is also possible to expect damage by creep processes when the parts are stressed at this relatively high temperature. That is why an experimental data on combination of high temperature corrosion and creep of candidate materials are essential for designers.

Two low alloy steels of type 0.3Mo and 2.5Cr1Mo, three austenitic steels of type 18Cr10NiTi, 25Cr18NiAl and 25Cr18NiSi and Fe-base alloy 28Cr45Ni2.7Si were crept at 500°C under different stresses before and after long exposure time at temperature 500°C in oxidizing-sulphidizing atmosphere consisted of in wt.% as follows: 34%H₂+34%CO+16.5%CO₂+15%H₂O +0.5%H₂S. From the results follows that the creep life calculation of parts exposed to aggressive corrosive environment could be based upon the original material characteristics when the changes of reduction of the load-bearing cross section area due to corrosive damage are accounted.

Key words: heat resistant materials, high temperature corrosion, creep, lifing.
THE ROLE OF MATERIALS IN MAXIMIZING THE ENERGY UTILISATION FROM SOLID WASTE FUELS - RECENT DEVELOPMENTS IN MATERIAL OPTIMIZATION AND PROCESS DESIGN

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Abstract

Energy utilisation from thermal waste treatment can be an important factor in reaching the goals of the 1997 Kyoto conference for reduction of greenhouse gases. High temperature corrosion of heat exchanger currently can cause operating problems and lower efficiency of incineration plants compared to fossil power plants. Laboratory and field investigation during COST-programme and failure case analyses led to the formulation of a mechanistic model for the formation of the corrosive flue gas and the interaction between flue-gas, deposits and the metal surfaces. The relevant parameters of the flue gas are described and their effects are quantified using a model flue gas. A corrosion mechanism is deduced from the analyzed samples. The possible improvements by different materials selection for evaporator and superheater tubes is described based on field tests and operators experience. The need and potential of further work is outlined.
INCREASE OF WASTE INCINERATOR POTENTIAL
BY ADVANCED SUPERHEATERS

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Abstract
Due to variations in waste and the increasing heating value, the chemical and thermal load of superheaters in waste-to-energy plants is high, resulting in severe corrosion and very limited life times. The objective of this collaborative project was to improve superheaters, by the selection of potential materials or coatings. Candidate materials and coatings were tested on a laboratory scale and in practice. Tube samples were welded in a 400 °C/40 bar superheater. A total exposure time of 8370 hrs. was reached. Plant conditions were quite severe, resulting in corrosion rates of more than 3 mm/year for the reference material 15Mo3. The advanced materials are able to increase the availability, to extend the lifetime with a factor of 5 to 10. Based on thermodynamics for potential materials extrapolations were made for various temperatures and operation times. Advanced materials offer the potential to make systems more tolerant to variations, to increase the availability, and to apply higher steam conditions.

Keywords: corrosion, waste incineration, superheaters, resistant alloys, coatings
CORROSION TESTING OF SUPERHEATER MATERIALS FOR USE IN WASTE AND BIOMASS FIRED COMBINED HEAT AND POWER PLANTS

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ABSTRACT
The project involved testing of two test superheaters at a waste-fired Combined Heat and Power plant. The purpose of the tests was to find suitable superheater materials, which allow higher steam temperatures.

Six alloys were selected for corrosion testing. The registered corrosion rates can be resumed in a calculation of life expectancy. For a tube with a wall thickness of 7 mm, the following lifetimes can be estimated: 252 MA: 8.2 months; AC 66: 8.1 months; TP 347: 6.8 months; X20CrMoV121: 6.1 months; FeCrAl: 2.8 months; 10CrMo910: 3.5 months.

A significant result of the work performed is thus that the solution to the high steam data in waste-fired plants is unlikely to be found using high alloyed steels. A more probable way will be to change the plant design so the superheater tubes are not exposed to high temperatures and a high chloride content in the flue gas at the same time.
PERFORMANCE OF AN IRON BASED ODS ALLOY IN A BOILER ENVIRONMENT

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Abstract

The mechanically alloyed ODS (oxide dispersion strengthened) materials have been commercially available only relatively recently. These alloys show generally good simultaneous resistance to creep and oxidation, and can withstand prolonged exposure at temperatures of up to 1000 - 1100°C. Practical applications would require reliable joining, while the ODS alloys cannot be e.g. fusion welded. In addition to non-conventional joining, practical use of ODS alloys requires demonstration in real plant service. For these reasons, pilot applications were sought in 1995-96 from Finnish boiler plants. To limit the cost impact, only iron-base rather than nickel base ODS alloys were considered.

Using three commercial filler materials, brazed joints were tested in short-term shear, shear creep and multiaxial creep for the iron-based PM 2000 ODS alloy, the reference Ni-based 45-TM alloy, and their dissimilar metal joints. Shear creep testing results of brazed ODS/ODS- and ODS/45-TM joints at temperatures of 800-900°C showed that with the nickel based BNi-5 and the palladium based Pd-40Ni filler metals the joint strength is considerably lowered with decreasing stress or strain rate. The Pd-40Ni appears somewhat stronger in creep than BNi-5 at 800°C, but the strength values converge at low stresses or temperatures above 900°C. In comparison, the Ag-4Ti braze is unsuitable for service temperatures above 600°C. No significant difference in the shear creep strength was found between the base materials, whether PM 2000 ODS, 45-TM or their dissimilar combination.

The specimens for creep testing under internal pressure were made with similar cross section dimensions to components of industrial heat exchangers. In spite of the selected joint geometry and initial difficulties in producing gas tight test joints, the results suggest that a creep strength comparable to those of the shear creep specimens can be achieved. Nevertheless, this creep strength level is expected to be much less than that of the ODS base material at very high temperatures, i.e. above 900-1000°C. Thus, for heat exchangers operating at very high temperatures it appears advisable to design brazed joints so that they are located outside the hottest regions.

For a service demonstration, an uncooled plate section of a boiler air nozzle, originally made of 253 MA, was replaced with the PM2000 ODS material at the Mussalo coal fired power plant of Pohjolan Voima in Kotka, Finland. After about one year, the ODS material has performed considerably better than the original nozzle material, showing no visible material loss, warping or surface oxidation. In this case the ODS material proved to be a cost effective solution in spite of the initial material cost.
EVALUATION OF THE EROSION-CORROSION RESISTANCE OF COATED METALLIC MATERIALS FOR CFBCs APPLICATIONS

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Abstract
Circulating fluidised bed combustors (CFBC) allow to burn a wide variety of fuels and to meet the restrictive pollutant emission requirements. However, materials, refractory as well as metallic, are a source of concern as their are responsible for outages and high maintenance costs. Erosion-corrosion resistant coatings are considered to improve the service life-time of the metallic substrate and to replace refractory linings wherever possible.
The erosion-corrosion resistance of coated materials has been measured on appropriate benches for 50 hours, that simulate representative conditions of a CFB environment. The influence of the following operating parameters was assessed: temperature, particle velocity, nature of the particle etc. The results were analysed by profilometry and micrographic studies and showed the complexity of the involved mechanisms. Besides, coatings are shown to improve the erosion-corrosion resistance comparatively to the bare substrate.

Keywords: erosion-corrosion, coatings, fluidised bed
Corrosion resistant coating materials
for heat exchanger tubes in waste incineration plants

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The heat exchanger tubes in waste incineration plants suffer from severe corrosion due to HCl in the flue gas and the formation of aggressive melts in the sulfate and chloride containing deposits on the surface of the tubes.

Low alloy steels exhibit poor resistance because iron is strongly affected by the chlorine catalysed active oxidation, which is one of the main metal consuming processes under these conditions. Even tubes made of high alloy steels, e.g. AC 66, a 27/32 Cr/Ni-steel, reach only unsatisfactory life times. The chromia or spinel layers formed on these materials are fluxed by the molten salts and passivation does not occur. Some Ni-base alloys exhibit better resistance, but the high price for nickel prohibits their use as tube material.

Since the corrosion processes only affect the surface and surface near zone of the tubes, coating these components seems to be a promising way of protection and the low demand on the mechanical properties of the coating material allows high contents of embrittling elements such as Cr and Si, which are beneficial for high temperature corrosion resistance. Furthermore, the use of low alloy substrate material coated with a corrosion resistant Fe-base alloy might be the most economic solution in spite of the additional costs involved by the coating of the tubes.

Fe-Cr and Fe-Cr-Si model alloys and commercial steels were embedded in deposits stemming from the heat exchanger tubes of a waste incineration plant and exposed at 600 °C in HCl-containing atmospheres, in order to simulate the waste incineration environment. The material degradation was characterized by the mass loss of the specimens after descaling of the corroded specimens. The experiments have shown that Fe-Cr-Si-alloys are much more corrosion resistant than AC 66 and Alloy 625.

The testing of thermal sprayed coatings of Fe-35Cr-5Si produced by atmospheric plasma and flame spraying such as HVOF in the simulated waste incineration environment revealed a strong dependence of the corrosion resistance on the structure and the arrangement of enclosed oxides within the scales. A structure of fine metal lamellae separated by oxide bands is detrimental for corrosion resistance. The available amount of chromium within the lamella, which is essential for corrosion resistance, is very limited. The oxide hinders the chromium supply from the underlying material and the corrosion and fast growing non-protective scales form. If the lamellae are wider, considerably higher amounts of oxides are tolerable.

The HVOF process seems to be most suitable for the deposition of the material because of the low oxide content of the coatings resulting from the low residence time in the burning gas. In addition, coarse lamellar coatings with a tolerable oxide content are produced by flame spraying.

In the laboratory experiments the corrosion rates measured for the commercial alloys are in the range of those observed in the final superheater section of waste incineration plants, so that conclusions on the corrosion resistance in such plants can be drawn. In the case of the final superheater, coating with Fe-35Cr-5Si allows a reduction in thickness of the coating of 80 % compared to Alloy 625, which is in use as corrosion protective coating in waste incineration plants.

Therefore, Fe-35Cr-5Si-coatings are a favourable way to protect low alloy steel tubes in waste incineration plants against high temperature corrosion resulting from HCl in the flue gas and molten sulfate/chloride mixtures in the deposits on the surface of the tubes. The HVOF spraying and flame spraying are suitable for the production of such coatings.
CERAMIC HEAT EXCHANGE APPARATUS FOR HIGH-TEMPERATURE GAS TURBINES

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ABSTRACT
Increasing gas-turbine unit (GTU) effectiveness can be achieved at combination of the high gas temperature at inlet (TIT=1500-1600°C) with heat regeneration (regeneration ratio E=0.75-0.85). This consideration promotes development of airheaters (AH) applicable for a long-term operation at the gas temperature exceeding 1000°C. To manufacture high-temperature heat exchange cells (HC) of such AHs, a structural ceramic material “SUGRAV” is utilized. Along with the high heat resistance property, this material has actually no shrinkage, does not need a diamond machining, ensures a strong and tight jointing of parts by the diffusive welding, does not oxidize up to 1200°C.
Brazing of SiC using the BraSiC® process for chemical and thermal applications

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Abstract

Totally new, BraSiC® filler alloys are particularly well suited to the joining of silicon carbide based materials (Sintered SiC, Si-SiC, SiC - SiC composites). Properties of the brazed joints are very close to those of SiC itself in terms of mechanical strength, temperature and corrosion resistances. Very flexible, the BraSiC® process allows the manufacturing of large components of complex geometry. Furthermore, the outstanding thermal properties of SiC opens to this ceramic a large field of applications in heat exchanger’s technology. The possibility to manufacture a SiC heat exchanger using the BraSiC® process has therefore been validated. A heat exchanger prototype has been fabricated and thermal tests have demonstrated the excellent resistance of the brazed joints for gas temperatures up to 1000°C.
MECHANICAL PROPERTIES OF HIGH TEMPERATURE CORROSION SCALES ON MATERIALS FOR HIGH TEMPERATURE HEAT EXCHANGERS

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Abstract
In order to develop reliable life prediction methodologies there is a requirement for appropriate data to support any predictive model. This paper presents a set of data for scales grown on the ODS alloy, PM2000, during oxidation in air at 1100 and 1150 °C. The data represent the parameters required during development of models for quantitative assessment of scale breakdown in this alloy.

Growth kinetics showed that the alloy underwent sub-parabolic oxidation. The scale growth rate was within the scatter band observed in previous studies of this material. The scales formed were uniform and consisted primarily of alumina.

Growth stresses in the oxide were low (-390 MPa). The implication is that creep relaxation in the substrate at the growth temperatures was rapid. This hypothesis is supported by the observation that residual stresses in the oxide after cooling to room temperature were similar for scales grown at 1100 and 1150 °C, -4.09 and -4.07 GPa respectively.

Hardness and Young's modulus of the oxide scale and substrate were measured using nanoindentation. The values obtained were independent of oxidation conditions showing that the structure and composition of the oxide is independent of oxidation conditions and that the substrate is not subject to thermal softening with the range of conditions used in this investigation.

Attempts to measure failure strain of the oxide using flexural loading were unsuccessful. Deformation was localised around the loading points and was not transmitted to the specimen gauge length. An improved test technique to measure this property is required.

Scale adhesion was characterised using scratch testing and indentation. Scratch testing showed qualitatively that the scale was adherent. This observation was confirmed by the indentation test were high values for the interfacial toughness (170 to 960 J m²) and fracture toughness (8 to 20 MN m¹/₂) were obtained. These values are higher than those obtained in previous work on alumina scales although the precise reason is not clear.
INFLUENCE OF PROCESSING ON MECHANICAL PROPERTIES OF MA 956 ALLOY

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Abstract

The microstructural characteristics (grain size and texture) and the mechanical properties at room temperature of MA 956 after different processing conditions have been investigated. The material was supplied in three conditions: hot isostatically pressed (HIP), hot extruded +1330°C/1 h and hot rolled. Two annealing treatments: 1100°C/100 h and 1330°C/1 h were performed on the hipped and hot rolled materials to observe the effect of the thermomechanic history on their final microstructure. In the hot extruded condition, the initial strong <110> fibre texture evolves towards a very strong <111> texture after 1330°C/1 h treatment, whereas in the hot rolled condition the initial fibre texture, with <110> and <100> components, results in a <100> after the same thermal treatment. The difference between the final texture of the extruded and rolled materials can be attributed to differences in the volume fraction of primary grains with <100> and <111> orientations. Clear differences in the mechanical properties along the longitudinal direction are observed, which results from the very pronounced texture developed. The MA 956 in the hot-extruded plus annealing at 1330°C/1 h presents the highest Young's modulus and proof stress.
FAILURE MODES OF ALUMINA SCALES ON FeCrAlRE ALLOYS

J.P. Wilber, M.J. Bennett*, J.R. Nicholls

Paper will be distributed at the meeting.
HIGH TEMPERATURE MATERIALS IN THERMAL WASTE TREATMENT PLANT APPLICATIONS: CORRELATION OF PLANT PERFORMANCE DATA WITH SIMULATED LABORATORY TESTS
G.K. Großmann, J. Klöwer

Paper will be distributed at the meeting.
Poster Presentations
C1 – C72
A COMPARATIVE INVESTIGATION ON THE THERMO-MECHANICAL FATIGUE BEHAVIOUR OF THREE NICKEL-BASE SUPERALLOYS

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Abstract
The thermo-mechanical fatigue behaviour of three nickel-base superalloys – IN738LC, CM247LC-DS and SRR99 – is compared for the out-of-phase cycle between 600–900°C. The results show that SRR99 presents a better TMF resistance as compared with the other two alloys. In fact, for a 1.0% mechanical strain range, the life observed for SRR99 is 2 times longer than for CM247LC-DS and 50 times longer than IN738LC. The large difference between the life observed for the polycrystalline alloy in comparison with the two others is due to physical and mechanical properties, mainly the modulus of elasticity and the yield strength. However, this difference in life is much smaller when the inelastic strain range or an energy based criterion is used to correlate the TMF life. Therefore, it seems that the latter are more adequate to take into account the TMF behaviour of these alloys.

Keywords: superalloys, thermo-mechanical fatigue, out-of-phase.
DEVELOPMENT AND CHARACTERISATION OF A HIGH STRENGTH SINGLE CRYSTAL SUPERALLOY - SMP 14

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Abstract
The single crystal nickel-based superalloy SMP 14 was developed by the CSIR, in conjunction with Ross & Catherall Ltd, for turbine blade and vane applications. It was designed to provide an equivalent temperature capability to current second generation single crystal alloys together with satisfactory microstructural stability and processibility. SMP 14 is currently under evaluation by European Gas Turbines Ltd. This paper summarises the work to date carried out within the test programme of the COST 501/III - WP14.SC Subgroup.
Improved Performance CMSX-4\textsuperscript{®} Alloy Turbine Blades Utilising PPM Levels of Lanthanum and Yttrium

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ABSTRACT
Turbine inlet temperatures (TITs) have now reached 1650°C (3000°F) at maximum power for the latest large commercial turbofan engines, resulting in high fuel efficiency and thrust levels approaching or exceeding 445 kN (100 000 lbs.). High reliability and durability must be intrinsically designed into these turbine engines to meet operating economic targets and ETOPS certification requirements. This level of performance has been brought about by a combination of advances in air cooling for turbine blades and vanes, 3-D computerized design technology for stresses and airflow and the development and application of rhenium (Re) containing, high $\gamma'$ volume fraction nickel-base single crystal (SX) superalloys, with advanced coatings, including prime-reliant ceramic thermal barrier coatings (TBCs).

At high gas temperatures, several issues are critical to turbine engine performance retention, blade life and integrity. These are tip oxidation in particular for shroudless blades, internal oxidation for lightly cooled turbine blades and TBC adherence to both the airfoil and tip seal liner. A team approach has been used to develop an improvement to CMSX-4\textsuperscript{®} alloy which contains 3\% Re, by reducing sulfur (S) and phosphorus (P) levels in the alloy to < 2 ppm, combined with residual additions of lanthanum (La) + yttrium (Y) in the range 10-30 ppm. Results from cyclic, burner rig, dynamic oxidation testing at 1093°C (2000°F) show thirteen times the number of cycles to initial alumina scale spallation for CMSX-4 [La + Y] compared to standard CMSX-4. CMSX-4 (ULS) [La + Y] HP shroudless turbine blades are scheduled to commence engine testing in mid 1998.

Keywords: CMSX-4, Turbine, Durability, Lanthanum and Yttrium.
MODELLING OF THE MECHANICAL BEHAVIOUR OF THERMOMECHANICALLY LOADED CMSX-4

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Abstract
The aim of the present work is to investigate superalloy blades for the first rotor stage in gas turbine. Single crystal blades exhibit an anisotropic deformation behaviour. They are subjected of triaxial stress fields induced by complex cooling systems. The prediction of their deformation behaviour requires constitutive equations. The γ/γ′ microstructure evolution during the life time modifies the material properties and has to be taken into account in the constitutive equations. For modelling anisotropic, viscoplastic behaviour of single crystal blades taking into account the evolution of the microstructure, a microstructure dependent, orthotropic Hill’s potential, whose anisotropy coefficients are connected to the edge length of γ′ particles, is applied. The shape of γ′ particles remains cubic. Testing at low temperatures, the microstructure-dependent potential leads to the cubic version of the Hill’s potential. The γ′ particles coalescence to form rafts at high temperatures (above 850°C), so that the viscoplastic response of the superalloy is continuously modified. Rafting reduces the creep resistance of <001>-orientated specimens, but does not occur in <111>-orientated specimen. Therefore there is an anisotropy change between <001> and <111>, which is successfully simulated using the microstructure-dependent model.

Keywords: CMSX-4, microstructure, constitutive equations, γ′ rafting, deformation modelling
AN INVESTIGATION OF THE ANISOTROPY OF THE SECONDARY CREEP RATE IN CMSX-4

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Abstract
Secondary creep data in three directions for CMSX-4, with data for other single crystals, were treated with a multi-batch fitting procedure so as to seek common trends over a wide range of stress and temperature while revealing the batch variability within the CMSX-4 class as well as intrinsic (fitting) scatter. It was concluded that anisotropy, while strong at high stresses, becomes weak or even absent at levels characteristic of power turbine applications. Also, though CMSX-4 has less batch variability than equiaxed materials, single crystal intrinsic scatter is greater and there is similar overall scatter for CMSX-4.

Keywords: single crystal, secondary creep rate, anisotropy, extrapolation, scatter, variability
Creep-Fatigue Behaviour of Polycrystalline and Single Crystal Nickel Base Superalloys IN738LC and SC16

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Abstract
Creep-fatigue behaviour of a polycrystalline superalloy IN738LC, a widely used blade material in land-based gas turbines, and a single crystal superalloy SC16 developed to replace the former have been investigated at 1223 K. Both the alloys have similar chemical compositions and initial microstructures. The mechanical tests were conducted on a servohydraulic MTS testing system at a cyclic strain rate of $10^{-3}$ s$^{-1}$ and constant total axial strain amplitudes of 0.4 %. The stress was kept constant (hold stress) only in the tensile part of the cycles. Different hold stresses (150 – 230 MPa) were used in the present study. Both the alloys show qualitatively a similar deformation behaviour: In the compressive part of the cycles a stable cyclic stress response was observed under all test conditions. The stress amplitude in compression increases with decreasing hold stress. The average creep rate during the hold periods as a function of number of load cycles shows a three stage behaviour: A rapid increase in the creep rate in the first stage. The second stage is characterised by a much slower increase in the creep rate with increasing number of cycles. In the last stage, the creep rate increases again rapidly. The cyclic lives of polycrystalline superalloy IN738LC (a few hundred cycles) are much shorter as compared to those of single crystal superalloy SC16 (about 4000 cycles) under the same test conditions. Besides, the single crystal alloy SC16 shows a weaker dependence of cyclic life on hold stress levels. The larger cyclic life of the alloy SC16 is obviously related to the absence of high angle grain boundaries in the alloy.

Keywords: Creep-fatigue, deformation, cyclic life
DESIGN OF A THIRD GENERATION
DS SUPERALLOY TMD-103

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Abstract
A third generation DS superalloy with creep strength as high as the second generation SC superalloys was developed. The alloy TMD-103 was designed by simply adding grain boundary strengthening elements, carbon and boron, to a third generation SC superalloy TMS-75 containing 5wt% Re. The alloy was cast to columnar grained directionally solidified structure with solidification rate at 200 mm/h. Creep test was performed after solution and aging heat treatments. Typical creep rupture lives at 900°C-392MPa and 1040°C-137MPa being 519 h and 884 h, respectively, which were equivalent with CMSX-4. A burner rig test showed a good hot corrosion resistance comparable with IN-792Hf. A DS hollow blade of a 2000KW class industrial gas turbine was successfully cast with TMD-103.
THIRD GENERATION SINGLE CRYSTAL SUPERALLOYS WITH EXCELLENT PROCESSABILITY AND PHASE STABILITY

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Abstract

Third generation single crystal superalloys with excellent processabilities and phase stabilities were developed. Using NRIM Alloy Design Program with help of Cluster Variation Method computer program based on statistical thermodynamics, an alloy TMS-75 containing 3wt% Cr, 5wt% Re, etc, was designed. The alloy had a wide solution treatment windows (≤ 40°C), suppressed TCP formation tendency and a high creep strength. Typical rupture lives at 900°C -392MPa and 1040°C -137MPa being 961 h and 1526 h, respectively. A laboratory scale hot corrosion test showed a very good hot corrosion resistance as well. It was also found that an Ir addition to TMS-75 further improves the phase stability.

Keywords: Third Generation Single Crystal Superalloy, Processability, Phase Stability, Creep, Hot Corrosion
DEVELOPMENT OF A NEW Ni-BASED SINGLE CRYSTAL SUPERALLOY FOR LARGE SIZED BUCKETS

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Abstract
This paper proposes to solve the problem of grain defects which occur in single crystal buckets or vanes of industrial gas turbines. At first, the most promising combination of grain boundary strengthening elements was investigated by considering creep-rupture strength of Ni-based directionally solidified superalloys in both longitudinal and transverse directions. Next, the most promising combination of W, Nb and Ta additions was examined with respect to phase stability and creep-rupture strength along the longitudinal direction. Finally, the B content was determined with respect to solution heat treatment stability. At a particular stress range, the new alloy; YH61 (single crystal) shows similar creep-rupture strength to one of the 2nd.-generation single crystal superalloys, although YH61 contains higher level of the grain boundary strengthening elements.

Keywords: Superalloy, Single Crystal, Low Angle Boundary, High Angle Boundary
HIGH PERFORMANCE AND HIGH COMPLEXITY NET SHAPE PARTS FOR GAS TURBINES: THE ISOPREC® POWDER METALLURGY PROCESS

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Abstract
ISOPREC® is a powder metallurgy process in which a highly sophisticated mould is filled with the powder and further densified through a HIP cycle. After compaction, the mould is mechanically or chemically removed, and a net shape part is obtained.

The large and complex deformations which are involved in the densification of the powder cannot be predicted manually (more than 30 % of the initial volume is eliminated). A modelling tool is under development. Its data base is progressively enriched with the properties of different mould and powder materials, in order to increase computation accuracy and minimize trial-and-error experiments. Comparisons between calculated and manufactured shapes are presented.

Examples of application of this technology to Inconel 625, Ti-6-4 and A316LN are presented. High dimensional accuracy and mechanical performance are obtained for complex parts, therefore minimizing cost and production cycle time for such high level components.

Keywords: Powder metallurgy, Hot Isostatic Pressing (HIP), Inconel 625, titanium base alloy, A316LN
HIGH TEMPERATURE MEASUREMENTS OF $\gamma'/\gamma$ LATTICE MISFITS IN THIRD GENERATION Ni-BASE SUPERALLOY

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Abstract
The lattice misfit of a third generation single crystal superalloy, TMS-75, was measured with a powder sample (at R.T. $\sim 1100^\circ$C) and a bulk sample (at R.T.) by X-ray diffractometry. The lattice misfit obtained with the powder sample changed from positive to negative as the temperature increased; 0.16% at R.T. and -0.14% at 1100$^\circ$C. With the single crystal bulk sample, a 300 superlattice and a 400 fundamental reflections were accurately measured at R.T. with a parallel X-ray beam mode using Ge(111) channel-cut monochromator. The 300 reflection was resolved into two peaks ($\gamma'$ and $\gamma'$) probably due to the coherency strain between $\gamma$ and $\gamma'$ phases. The 400 reflection was resolved into four peaks correspond to $\gamma$ and $\gamma'$ phases. The lattice misfit thus obtained from the bulk sample was about -0.06% at R.T., which is slightly shifted toward negative compared with that of the powder sample.

Fig. 1  Temperature dependence of the lattice misfit by the powder X-ray diffractometry.

Fig. 2  300 reflection of TMS-75 bulk SC sample at R.T.

Fig. 3  400 reflection of TMS-75 bulk SC sample at R.T.
Design of high Re containing single crystal superalloys for industrial gas turbines

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Abstract
Re addition to Ni-base superalloys tend to enhance the precipitation of topologically closed packed (TCP) phase. In this paper, characterization of TCP phase and the influences of TCP phase on creep rupture life were studied. From analytical electron microscopy (AEM) observation, TCP phase was found to be a sigma phase containing high concentration of Re, Mo and W elements. TCP phase tended to precipitate easily at higher temperature and there was no preferential temperature of precipitation up to 1100°C. Creep rupture life was reduced proportionately as volume fraction of TCP phase increased. Phase computation (PHACOMP) results did not necessarily correlate well with experimental results.
THE LOCATION OF ATOMS IN Ir-CONTAINING Ni-BASE SINGLE CRYSTAL SUPERALLOYS

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Abstract

In order to develop higher efficiency engines, there are still considerable efforts being devoted to enhance the temperature capabilities of Ni-base single crystal superalloys. To enhance heat resistibility, the superalloys usually contain several alloying elements such as Cr, Co, Mo, W, Ta etc. Among these elements, Re has recently been paid much attention because of its contribution to improve both the creep and corrosion properties. However, Re addition also assists the formation of TCP phase, partly because Re has a low diffusibility, which results in the segregation of Re atoms where precipitation of TCP phase easily occurs, and partly because the solubility limit of Re in Ni is rather low due to the difference in atomic structures between Re (hcp) and Ni (fcc). On the other hand, addition of Ir in Ni-base superalloys is of particular interest. Since Ir and Ni have a complete solid solution system, we expect a fairly high amount of Ir can be alloyed compared to Re. It should also be noted that there have been no reports about Ir-containing Ni-base superalloys. The main objective of this study is to investigate the microscopic characteristics of some Ir-containing superalloys using atom probe field ion microscopy (APFIM) and transmission electron microscopy (TEM). The derived data were also compared with the numerical estimations obtained from the cluster variation method (CVM) and the Monte Carlo Simulations (MCS).

It is found by preliminary APFIM investigations that Ir has a small preference to partition into the γ phase and occupy for the Al sites in the γ' phase, which were in agreement with numerical estimations derived by CVM and MCS. However, the partitioning preference to the γ phase is less stronger than that of Re and Mo. The typical configurational features of Ir, such as enrichment at interfaces which were often observed in Re-containing alloys, have not been observed in Ir-containing alloys. In this study, these microstructural characteristics of Ir-containing alloys will be discussed compared with those of other alloys systems such as Ir-free alloys and Re-containing alloys.
PRECIPITATE SHAPE DEPENDENCE OF STRENGTH IN IR-BASE REFRACTORY SUPERALLOYS

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Abstract

The microstructure and compression strengths of Ir-base binary alloys (Ir-X, where X is V, Ti, Ta, Nb, Hf, or Zr) at temperatures between room temperature and 1800 ºC were investigated. Several Ir-base alloys displayed superior strength throughout the temperature range. An fcc and L1₂ two-phase structure was observed in the Ir-based alloys by a transmission electron microscope and is believed to be an important element of the strength performance. Precipitate shape was observed to depend upon the lattice parameter misfit between an fcc matrix and L1₂ precipitates. Cuboidal L1₂ precipitates formed in the Ir-Nb and Ir-Ta alloys with lattice misfit about 0.3%. Plate-like precipitates were formed in the Ir-Hf and Ir-Zr alloys with lattice misfit about 2%, and these precipitates formed a three-dimensional maze structure. The strength of these alloys increased with increasing lattice misfit. Precipitation hardening was investigated in the Ir-Nb and Ir-Zr alloys, but was larger in the Ir-Zr alloy. The effect of precipitate shape and coherency strain on precipitation hardening are discussed in terms of lattice misfit.

Keywords: precipitation hardening, compression strength, high temperature materials, fcc and L1₂ two phase coherent structure
Hot Corrosion Properties of Ni-base Single Crystal Superalloys in Burner Rig Test

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Abstract

Responding to the demand of increase in the gas turbine inlet temperature, Ni-base single crystal superalloys have been used for turbine blade and vane because of their excellent high temperature properties. High resistance to hot corrosion caused by impurities in fuel is required for hot gas path components of the land-based industrial gas turbine. However, there are a few systematic studies for hot corrosion (sulfidation in particular) behavior of single crystal superalloys in severe corrosion environments such as combustion atmosphere in heavy oil-fired gas turbine. In this study the hot corrosion behavior of commercial Ni-base single crystal superalloys (CMSX-2, CMSX-4 and CMSX-10) was investigated using burner rig tests which partially simulate the combustion gas atmosphere in heavy oil-fired gas turbine. Some equiaxed-grain alloys were used as the comparison alloy. In the accelerated hot corrosion test at 900°C the hot corrosion resistance of the single crystal superalloys was slightly lower than or equal to that of higher Cr containing equiaxed-grain alloys. At higher temperature of 1050°C, all single crystal superalloys were attacked severely and catastrophic corrosion was taken place. The network structures of inner oxides were observed in the single crystal superalloys after hot corrosion test at 1050°C. However, in accelerated oxidation test at 1200°C, the single crystal superalloys posses excellent oxidation resistance. Considering the results of this study, we proposed a new type of mechanism of hot corrosion of the single crystal superalloys.

Keywords: hot corrosion, Ni-base superalloy, single crystal, burner rig test
EFFECT OF GRAIN BOUNDARY ORIENTATION ON CREEP AND FRACTURE BEHAVIOR OF A DIRECTIONALLY SOLIDIFIED NICKEL-BASE SUPERALLOY

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Abstract
The effect of grain boundary orientation on creep and fracture behavior of a directionally solidified Ni-base superalloy used for blade and vane in advanced gas turbine engine had been investigated at 1253K in the stress range of 130-190 MPa. The results showed that three orientation specimens, in which the columnar grain boundaries were oriented longitudinally, transversely, and 45 degree to the applied stress axis, had similar shape of the creep curves with a small primary and a dominant tertiary creep stages. It was found that the creep deformation mechanism in three orientation specimens was same, which was controlled by dislocation climb by-pass process. The strain to fracture in longitudinal orientation specimens was much higher than that in transverse and inclined orientation specimens. In terms of SEM observations, it was suggested that this difference of the creep fracture behavior came from the change of creep fracture mechanism from the transgranular mode in longitudinal orientation specimens to the intergranular failure in the other orientation specimens.

Keywords: directionally solidified Ni-base superalloy, grain boundary orientation, high temperature creep and fracture behavior
High Temperature Double Shear Creep Deformation of Ni-based Superalloy Single Crystals

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Abstract
High temperature (>1273 K) creep anisotropy of single crystal (SX) nickel base superalloys of CMSX-6 and CMSX-4 was studied using a shear test technique. The results indicate that there is a dependence on crystallographic orientation of shear creep properties in both alloys for all testing conditions (T = 1293-1373 K, \( \tau = 85-100 \) MPa). In both materials, the smallest minimum creep rate was found for the \{001\}[100] crystallographic shear system. CMSX-4 is more creep resistant than CMSX-6. The apparent activation energy for creep in the stress and temperature range of this study is higher for CMSX-6 than for CMSX-4. An explanation of this effect is based on an Orowan back stress / rafting argument: dislocation loops which fill the narrow \( \gamma \) - channels experience an Orowan back stress determined by the channel width. As rafting proceeds the channel width widens. This effect is diffusion controlled and its temperature dependence gives an additional contribution to the apparent activation energy of creep which therefore naturally is higher than the activation energy of self diffusion. The effect is less pronounced, however, in CMSX-4 as compared to CMSX-6 because diffusion is slower in CMSX-4 due to the presence of heavy alloying elements (W, Ta and Re).

Keywords: shear, creep, CMSX-4, CMSX-6, creep anisotropy, minimum creep rate.
Fatigue crack growth of small cracks in the single crystal super alloys SC16 and CMSX-4

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Abstract
In the new generation of stationary gas turbines for electrical power generation, single crystal superalloys are used. With the new design of gas turbine components crack growth studies of small cracks in these alloys gain more and more importance. Fracture mechanics concepts for cracks smaller than 1mm with different crack shapes are very useful for prediction of crack propagation between two maintenance or inspection interruptions. In the present study the fatigue crack growth behaviour of the single crystal alloys CMSX-4 and SC16 was tested in air at 750 and 1000°C for two different crack shapes. There were only slight differences in the fatigue crack growth behaviour found between the corner and edge crack geometry. The main differences in the crack growth behaviour were worked out between the different alloys (γ'-content) as well as for the different test temperatures. Low temperatures and a high γ' content led to a change of the crack growth direction along {100} type crystal planes to {111} type crystal planes.
CREEP AND CREEP-FATIGUE BEHAVIOUR OF UDIMET 720 AT 850°C

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Abstract

The object of this study is to identify damage mechanisms operating at high temperature (850°C) in Udimet 720, a nickel-based superalloy strengthened by γ Ni₃Al precipitates. In addition to environmental effects, the extension of viscoplasticity may result in specific damage mechanisms, such as intergranular cavitation, wedge cracking and/or thermal coarsening of γ particles. The major mechanisms have been investigated using tensile smooth specimens, for creep and creep-fatigue loadings. The introduction of the relevant damage parameters in a model describing the viscoplastic behaviour of the material is tentatively discussed.

Keywords: creep, creep-fatigue, nickel-based superalloy, viscoplasticity
Fatigue crack growth and tensile deformation of the PM superalloy N18: microstructural investigations

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Abstract
The aim of the present work is to investigate the correlation between mechanical properties and microstructural mechanisms, controlling the deformation process, by means of transmission electron microscopy (TEM). The mechanical behaviour of the powder metallurgically (PM) produced, nickel base superalloy N18 has been examined at 700°C in laboratory air with strain rate controlled tensile tests at different strain rates and as crack growth tests, carried out as creep-fatigue tests. Additional crack growth tests have been carried out in vacuum. The microstructure was characterized in the undeformed and deformed states by means of TEM with the assistance of energy dispersive X-ray analysis (EDX) and energy spectroscopic imaging (ESI) to investigate the elemental distribution. The alloy exhibited different crack growth rates in vacuum and in air. For the tensile tests, viscoelastic or viscoplastic deformation behaviour, depending on the strain rate, was observed, with the creation of stacking faults for all deformation velocities and a decreasing dislocation density in the primary γ' with decreasing strain rate.
Creep and Microstructure of near $\gamma$-TiAl Intermetallics

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Abstract
Creep and microstructure of two near-$\gamma$ TiAl intermetallics are investigated and compared. Data obtained in tension and compression at temperatures 923-1100K and in the applied stress range 50-400MPa are presented. A pure $\gamma$-phase Ti-52at%Al crept at 1100K is brittle once the applied stress exceeds 150MPa. On the other hand, a two-phase $\gamma/\alpha_2$ fully lamellar Ti-48Al-2Cr-2Nb-1B (in at%) alloy exhibits a remarkable ductility at considerably lower temperatures. A conventional light microscopy, SEM and TEM were used to quantify the microstructure of the alloys before and after creep. Contrary to a grain growth, observed during creep of Ti-52at%Al alloy, a grain refinement due to recrystallization was found after creep in Ti-48Al-2Cr-2Nb-1B alloy. The difference in creep behaviour of the investigated alloys is attributed to a different intensity of dislocation glide, twinning and recrystallization, the microstructural processes which operate in the range of external conditions studied.
MICROSTRUCTURES, DEVELOPMENT OF DEFECTS, AND CREEP BEHAVIOUR IN A γ-TIAL BASED ALLOY FOR GAS TURBINE APPLICATIONS

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Abstract
The microstructure of a γ-based two-phase Ti-48Al-2W-0.5Si in different microstructural conditions was investigated, before and after creep testing. The creep tests were performed in air at constant load, and the applied stresses were between 80 and 325 MPa at temperatures from 700 to 850°C. Materials from creep testing to rupture reported in an earlier study, as well as interrupted at 1% creep straining reported here, were investigated. A variation in microstructure was found to depend on minor variations in chemical analysis, heat treatments and HIP-ing conditions between different materials. Scanning and transmission electron microscopy were used to study the microstructure and defect structures during creep deformation.

Keywords: creep cavities, dislocations, microstructure, structural instabilities, titanium aluminide
MICROSTRUCTURE AND CREEP RESISTANCE AT 650-750°C OF THE Ti-47Al-2W-0.5Si CAST ALLOY

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Abstract

Various batches of the Ti-47Al-2W-0.5Si cast alloy having small composition variations have been examined. The microstructure was found to vary with composition strongly, influencing the creep resistance. In particular the microstructure depends very critically on exact composition, on the solidification path and on the heat treatment region in the phase diagram.

Duplex microstructure material, consisting of lamellar $\alpha_2/\gamma$ colonies and globular $\gamma$ grains, is mainly described and seems to provide a good compromise of mechanical properties, specially when solidification occurs through the $\beta$ phase. When Al content is slightly low, the volume fraction of lamellar colonies increases greatly, improving creep resistance. Silicon content also plays an important creep strengthening role. The explored W content deviation does not seem to have a direct predominant influence on creep resistance, while it does affect the solidification path.

Fully lamellar microstructure, that is the most creep resistant but less ductile at room temperature, is also considered.

Aging at 800°C for more than one month definitely lowered the material creep resistance, shortened its creep life and coarsened its microstructure, in particular partially degrading the lamellar microstructure of duplex material to equiaxed $\gamma$ and $\alpha_2$. Aging at 650°C for 1000 h did not change the microstructure substantially and did not produce a weakening effect on creep.

The batch of duplex material containing the highest lamellar microstructure volume fraction, has very good creep resistance and should also have a good mix of various high temperature mechanical properties. Nevertheless the fully lamellar microstructure is the most creep resistant, but should be taken into consideration only when ambient temperature brittle behavior is tolerable.
HIGH TEMPERATURE FATIGUE BEHAVIOUR OF \( \gamma \)-TiAl BASE INTERMETALLIC ALLOY

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The fatigue behaviour of a new \( \gamma \)-TiAl base intermetallic compound with duplex microstructure, developed to obtain high creep resistance and good tensile properties, has been studied. Low cycle fatigue (LCF) and fatigue crack propagation (FCP) cast specimens of Ti –48Al – 2W were tested up to a temperature of 800°C with triangular wave shape. The influence of time dependent processes on fatigue resistance has been investigated adding a 300 s hold time at maximum load in the LCF tests and varying frequency in the 0.1 to 10 Hz range in the FCP tests. The influence of environment that has been recognised very important, on FCP has been analysed through a comparison of crack growth behaviour in air and in vacuum.

The LCF results show a slight reduction of fatigue life with temperature increasing and a marked influence of a 300 seconds hold time in tension at 800°C. The stress response is almost stable during the fatigue life and fracture occurs rapidly in few cycles as soon as crack initiation is present. The FCP results confirm the small influence of temperature on fatigue crack propagation rate (FCPR) up to 800°C with a maximum value at 700°C. The material is strongly affected by environment, as shown by vacuum tests. At 700°C FCPR is sensibly higher in air than in vacuum. A beneficial effect of creep processes at crack tip is observed when frequency is reduced.

The fracture surfaces of the tested specimens have been thoroughly investigated using scanning electron microscopy in order to correlate the fatigue behaviour to the microstructural features and to identify the main fracture mechanisms involved. Generally the fatigue crack starts on the external surface and propagates in transgranular mode without the presence of fatigue striations, due to the very low ductility of the alloy. In specimens tested with hold time some mixed intergranular – transgranular crack propagation zones are apparent.

Keywords: \( \gamma \)-TiAl aluminide, low cycle fatigue, fatigue crack propagation, environment, hold time
LOW CYCLE FATIGUE OF THE $\gamma$-BASED ALLOY
Ti-48Al-2W-0.5Si

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Abstract

Eight batches of the $\gamma$-TiAl alloy Ti-48Al-2W-0.5Si with a slightly varying compositions have been examined through fully reversed low cycle fatigue testing at two temperatures, 600°C and 700°C. The influence of a 300 s hold-time in tension at 700°C has also been investigated. The study has shown a large influence of the microstructure on the fatigue properties. A duplex fine grained microstructure has superior properties in comparison with a material low in aluminium with a coarse grained nearly lamellar structure. In addition, materials with the duplex structure show a much smaller scatter in test results. The results from the two temperatures tested are similar, i.e. the effect of temperature influence in this range is negligible. No effect of hold-time can be seen. The low cycle properties can be described with the well-known Coffin-Manson equation.

The strain controlled fatigue properties show a strong sensitivity to the strain range, an effect that can be attributed to the high Young’s modulus and the relatively low yield strength of the material which leads to inelastic straining and fatigue damage already at small strain ranges. The duplex material exhibits longer lives due to larger isotropic hardening and smaller Bauschinger effect, which lead to smaller inelastic strains and damage in each cycle. The scatter in fatigue test results is explained by the large influence of the microstructure and the anisotropic properties of the lamellar colonies. Fractography has shown that initiation often occurs between the lamellas in large lamellar colonies at the surface of the gauge length. The probability to have a lamellar colony with the lamellas oriented perpendicular to the loading axis producing premature failure is increased as the content of this microconstituent is increased.
HIGH TEMPERATURE FATIGUE PROPERTIES AND RELATED MICROSTRUCTURES OF GAMMA TIAI INTERMETALLIC ALLOYS

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Abstract

Fatigue properties of two gamma TiAl intermetallic alloys (those studied in COST 501/III W.P.14 and in COST 513) were measured in push-pull mode fatigue both at room temperature and at 700 °C using R- ratios of 0 and -1. The fatigue tests were carried out either to the fracture of the specimen or to $10^7$ cycles. The microstructures of the fatigued samples were characterized by transmission electron microscopy. The results show that the low cycle fatigue strength of the COST 501/III alloy is clearly higher at 700 °C than at room temperature. At 700 °C the R-value of -1 yields better low cycle fatigue properties as compared to the R-value of 0. At higher numbers of fatigue cycles at 700 °C the originally strongly twinned microstructure of COST 513 alloy is replaced by a highly dislocated microstructure without twins. The high temperature fatigue deformation seemed, however, to a certain extent to stabilize the twins in the microstructure.

Keywords: gamma titanium aluminides, high temperature fatigue, fatigue deformation, TEM microscopy
CREEP AND LOW CYCLE FATIGUE BEHAVIOUR OF A
γ - TiAl FOR GAS TURBINE APPLICATION

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Abstract

Intermetallic compounds based on titanium and aluminium, characterized by low weight, seem to be candidate for medium term applications in high temperature components for land-based gas turbines, in particular for last stage blading, where the service temperature does not exceed 750 °C. In this temperature range the titanium aluminides show a high specific creep strength, a quite high low cycle fatigue life and a good oxidation and corrosion resistance, whereas the lack of low temperature ductility and toughness has represented their main problem.

In the frame of the COST 501/R.III WP14 “Advanced Materials for Gas Turbines” Subgroup 1 “Intermetallics for GT Application” programme, an extensive experimental activity has been performed with the aim of evaluating the γ-TiAl in view of a possible application in last stage blading gas turbine.

In particular, the mechanical behaviour, in term of creep and low cycle fatigue resistance, has been evaluated on different delivery materials: isothermal creep rupture tests at 700 °C, with duration between 200 and 4000 h, and low cycle fatigue testing at 600 and 700 °C have been carried out. Microstructural investigations on the as received and tested materials have been performed.

The obtained results allow to draw the following remarks.

It has been observed an increase in the creep resistance for the duplex structure material with respect to the nearly lamellar one; in particular the last delivery material, with finer grain size, presented the best compromise between the creep strength and the rupture ductility. Moreover the density corrected strength of the TiAl seems to be comparable, if not better, to the creep resistance of IN738LC from literature.

Also the low cycle fatigue resistance resulted increased for the duplex material, even if a considerable scatter, probably due to differences in composition and microstructure, was present. The observed cycling hardening effect, coupled with the brittle crack propagation, was typical of the materials susceptible to crack initiation.
INFLUENCE OF STATE OF STRESS ON CREEP/FATIGUE FAILURE OF $\gamma$-TITANIUM ALUMINIDE TURBINE BLADE MATERIAL

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Abstract

This investigation formed part of the COST 501/III WP14 programme, to examine the mechanisms of 'creep/fatigue failure of $\gamma$-titanium aluminide' to evaluate the material for possible use in future turbine blade applications. The main objectives of the paper is to determine the influence of state of stress on the creep-fatigue failure characteristics of $\gamma$-titanium aluminide at 700°C. Four batches of the material were tested and a comprehensive testing programme by a number of laboratories was undertaken. The work involved mechanical testing and numerical analysis. In order to evaluate the effects of state of stress experiments were conducted on notched and un-notched tensile bars and crack growth testing of compact tension specimens of the $\gamma$-titanium aluminide at 700 °C. New techniques were developed to measure accurately the diametral strains at 700 °C over long periods. Subsequently metallographic examination was carried out on failed specimens. Secondly elasto-plastic-creep finite element analysis was performed on the notched bars with the different notch root radii to determine the state of stress in the notch root region. In addition the modelling the formation of damage and incorporation into the prediction of failure under Creep and Creep-Fatigue was performed for the notched bars.

Keywords: Gamma-Titanium, multiaxial stress, creep, fatigue
The Effect of Noble Element Additions on the Oxidation Resistance of $\gamma$-TiAl Based Alloys

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Abstract
The effect of small additions of Ag and Au on the high temperature oxidation of $\gamma$-TiAl based alloys has been investigated at 800°C in air by optical metallography, XRD and SEM/EDX. The results showed that Ag and Au additions lead to a significant reduction in the oxidation rate of $\gamma$-TiAl. The Au-containing alloys formed mixed $\text{Al}_2\text{O}_3$$/\text{TiO}_2$ scales while the Ag-containing alloys formed a thin, protective $\text{Al}_2\text{O}_3$ layer. The Al-depletion zone beneath this $\text{Al}_2\text{O}_3$ scale consisted of a single Z-phase layer which was doped with Ag. Beneath the mixed scale on the Au-containing alloys a thin layer consisting of Z-phase as well as Ti$_2$AlN and TiN precipitates was present. The excellent oxidation resistance of the $\gamma$-TiAl(Ag) alloys is believed to be due to stabilisation of the Z-phase by Ag and absence of Ti$_2$AlN precipitates in the sub scale Al-depletion zone.

Keywords: $\gamma$-TiAl, intermetallics, high temperature oxidation, Z-phase.
EARLY STAGES OF HIGH TEMPERATURE OXIDATION OF γ-TiAl ALLOYS: INFLUENCE OF W AND Si ADDITION

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Abstract

In this study the results of the isothermal oxidation behaviour in air and over the temperature range 700-850°C of γ-TiAl bulk alloys with additions of W (0-9.5 wt.%) and Si (0-0.4 wt.%) are reported. The specimens were prepared using an arc-melting apparatus starting from pure element powders (99.99%). The samples were tested using a thermogravimetric analysis in order to evaluate the oxidation kinetics. The microstructure and adherence of the protective scale to alloy substrate were investigated using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Auger Electron Spectroscopy (AES). In all investigated alloys the oxidation rates show the beneficial effect of the W and Si additions. The results of the study are used for a critical assessment of the oxidation mechanism and to suggest a possible approach for improving the scale adherence.

Keywords: Titanium aluminides, Oxidation, High Temperature Materials.
THE BEHAVIOUR OF PVD SIALN-TYPE COATINGS DEPOSITED ON γ-TiAl

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Abstract
SiAlN-type coatings up to 10 μm in thickness were deposited by magnetron sputter ion plating (MSIP) on two γ-TiAl alloys Ti, 47Al, 2W, 0.5Si at-% and Ti, 47Al, 2Nb, 2Mn at%, 0.8% TiB2. Coating parameters were optimised using reactive d.c. sputtering from a SiAl target in a nitrogen or methane atmosphere. The properties of the coatings were determined using X-ray diffraction, hardness, modulus, scratch, indentation and ductile brittle transition temperature measurements. High temperature X-ray measurements suggested that the coatings remained amorphous up to about 950°C. Scratch and Rockwell indentation tests indicated that the had inferior adhesion to MCrAlY overlay coatings, whereas ductile brittle transition temperatures were comparable with other overlay systems. Oxidation testing for 3300 h at 800°C in air showed that despite cracking during the initial thermal cycles significant protection was conferred to the γ-TiAl; evidently healing of the cracks occurred. Interaction with the substrate was slight after the long-term exposure at 800°C with some silicon interdiffusion.
The effect of thermo-mechanical processing and heat treatment on the microstructure and mechanical properties of orthorhombic alloys

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Abstract
The effects of thermo-mechanical processing and heat treatment on the microstructure and mechanical properties of a Mo bearing orthorhombic alloy has been evaluated. This study has shown that tensile strengths in excess of 1000MPa combined with plastic elongations >2% can be achieved by a three step ageing treatment. This three step ageing treatment is associated with an increasing volume fraction of orthorhombic phase. Significant changes in elastic modulus were also observed following the different heat treatments. Creep testing of the alloy showed that all the samples studied failed at strains <3.5%. This was attributed to the large grain size observed in the forged material. Creep testing of the β+ heat treated specimen demonstrated that the re-solutioning of the alpha-2 precipitates leads to higher secondary creep rates and shorter creep lives.

Keywords: Orthorhombic, processing, microstructure, mechanical properties.
CREEP BEHAVIOUR OF DIRECTIONALLY SOLIDIFIED Ni$_3$Al-BASED ALLOY

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Creep behaviour of directionally solidified (DS) Ni$_3$Al-based alloy with chemical composition Ni-10.6Al-8.3Cr-2.6Fe (wt.%) was investigated. The creep specimens were prepared by directional solidification in a modified Bridgman-type apparatus at a constant growth rate of $V = 4.17$ μm/s and constant temperature gradient at the solid-liquid interface of $G_L = 15$ K/mm under argon atmosphere. Before the creep tests the specimens were annealed for 100 h at 900°C in air. Constant stress creep tests were performed at the temperature range 777 to 877°C under tensile stresses ranging from 150 to 350 MPa in air. In addition, stress reduction experiments were conducted to study transient creep behaviour of the alloy.

The microstructure of DS alloy consisted of multiple eutectic grains. Within each grain, well aligned and equally spaced lamellae were observed. TEM and EDS observations revealed that the lamellae were composed of B2 type intermetallic compound NiAl(Cr, Fe) ($\beta'$-phase), some L1$_0$ type martensite ($\beta'$-phase) and b.c.c. type spherical Cr precipitates. The matrix was composed of L1$_2$ type intermetallic compound Ni$_3$Al(Cr, Fe) ($\gamma'$-phase), f.c.c. type Ni-based disordered solid solution ($\gamma$-phase) and fine lath-shaped Cr precipitates. During annealing in the temperature range from 750 to 900°C the as-grown lamellar $\gamma\gamma'$-$\beta$ structure transformed to $\gamma\gamma'$-$\alpha$ structure. This transformation was connected with an extensive precipitation of Cr particles. The microstructure of the creep specimens annealed before creep test at 900°C for 100 h consisted of the ordered $\gamma'$-matrix, lath-shaped Cr precipitates and small amount of disordered $\gamma$-phase. The lath-shaped Cr precipitates were uniformly distributed within the bands.

The creep curves exhibited short inverse primary creep stage. The steady-state creep stage was achieved at a creep strain of about 1% and extended up to a creep strain of about 10%. During the primary creep stage the creep rate first decreased with increasing creep strain. After reaching a minimum, the creep rate increased up to its steady state value. During tertiary creep stage the creep rate continuously increased up to a creep fracture. After a stress reduction the instantaneous creep rate was higher than the steady-state creep rate corresponding to the reduced stress.

The steady-state creep rate was found to depend on the applied stress and temperature. The power law stress exponent for steady state creep was measured to be $n = 4.1 \pm 0.1$ and the apparent activation energy for creep was calculated to be $Q_a = 316 \pm 9$ kJ/mol. The activation energy for creep is comparable with the activation energy for lattice diffusion of Ni in Ni$_3$Al (305 kJ/mol). The kinetics of the steady-state creep deformation within the studied temperature range was governed by the diffusion controlled dislocation climb over the Cr precipitates.

During the tertiary creep stage the creep specimens underwent extensive plastic deformation before fracture. The total elongation and reduction of area were function of applied stress and temperature and varied from 22 to 75 % and 20 to 50 %, respectively. The tertiary creep was accompanied with multiple necking in the gauge region. The necking was associated with an extensive formation of large slip bands and growth of large voids. Slip band formation followed by the growth and coalescence of voids along the slip bands and cavities at the columnar grain boundaries led to ductile fracture of the creep specimens.
A New Generation FeAl Alloy with Advanced Properties

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Ordered FeAl intermetallics are attractive materials for medium and high temperature industrial applications but their use have been restricted until now by their room temperature brittleness and their poor creep resistance. Powder metallurgy techniques have been used to develop a mechanically alloyed FeAl alloy, named FeAl40 Grade 3, with enhanced ductility and strength at both low and high temperatures. The improvement method combines ductilization by grain boundary strengthening, grain size reduction and oxide dispersion strengthening. The optimization of the elaboration process has led to a material with significant RT ductility (8%), excellent fatigue strength and improved creep resistance. At room temperature, yield strength is as high as 900 MPa and rupture strength reaches 1150 MPa. Specific stiffness is higher than that of most conventional engineering alloys including steels, superalloys, aluminum and titanium based alloys. Specific strength is equal to that of conventional titanium based alloys. In addition, the FeAl alloy has excellent corrosion resistance to oxidizing, sulfurlizing and carburizing environments up to 1000°C. Potential applications in aeronautical and automotive industries concern the substitution of steels and nickel base alloys for the fabrication of high speed rotating or moving parts, such as shafts or valves.
THERMAL FATIGUE BEHAVIOUR OF THE COMBUSTOR ALLOYS IN 617* AND HAYNES 230

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Abstract

The effect of thermal fatigue (TF) on the life time of the common materials for combustor parts, IN 617 and Haynes 230, has been tested, using single wedge specimens. Their leading edge was heated by induction and cooled by pressurized air between 200°C and 850, 950 and 1050°C, respectively. Under comparable temperature cycles and thermal gradients Haynes 230 showed a higher TF strength than IN 617. It is proposed that this advantage of Haynes 230 is primarily related to a slightly lower value of the relevant combination of properties (coefficient of thermal expansion, modulus of elasticity, thermal conductivity, ultimate strength at maximal operating temperature), while details of crack initiation and propagation also play an important role.

Severe embrittlement of IN 617 in the turbine operating condition reduced the TF life significantly, whereas aging in the laboratory furnace reduced the TF life in both alloys, only marginally.

Keywords: combustor, thermal fatigue, embrittlement
INFLUENCE OF THE MINIMUM CYCLE TEMPERATURE ON THE THERMAL-MECHANICAL FATIGUE BEHAVIOUR OF NICR22CO12MO9

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Abstract

In components operating at high temperatures thermal and mechanical loadings are induced due to start-ups, load changes and shut downs. Transient temperature fields in these operating phases produce complex stress and strain fields which may cause fatigue damages and therefore may be responsible for the failure of the entire system. Typical examples for this are gas turbines. Most of their components are subjected to combined thermal-mechanical loading. The combustion chamber, which is one of the highest loaded component of a gas turbine, is commonly made of the nickel base superalloy NiCr22Co12Mo9 (IN 617, Nicrofer 5020 Co). In the present study, the materials reaction and the microstructural changes due to thermal-mechanical fatigue with $T_{\text{max}} = 1123$ K and different $T_{\text{min}}$ are investigated under total strain control and compared to its isothermal total strain controlled fatigue behaviour at the maximum cycle temperature.

In the realized thermal-mechanical fatigue tests high dislocation and carbide densities are generated and the material shows cyclic hardening. On the other hand isothermal fatigue at the maximum cycle temperature causes a slight cyclic softening. Under thermal-mechanical loading the development of the fatigue damage depends on the phase relation between temperature and mechanical loading. In-phase loading causes tensile stresses at high temperatures whereas out-of-phase loading induces compressive stresses at high temperatures. Therefore, especially at lower $T_{\text{min}}$, in in-phase tests more intergranular damage is produced than in out-of-phase tests and the fatigue life is shorter. At $T_{\text{min}} = 473$ K the lifetime of an in-phase thermal-mechanical loaded specimen is even lower than that one of an isothermal with the same total mechanical strain amplitude at the maximum cycle temperature loaded specimen. This proofs how important it is to choose a suitable minimal temperature to perform thermal-mechanical fatigue tests.
TRACE OF THE EVOLUTION OF NICKEL-BASED
SUPERALLOYS
BY THE d-ELECTRONS CONCEPT

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Abstract

A variety of nickel-based superalloys have been developed for structural applications in
high-temperature and corrosive environments. Their chemical compositions have been
optimized so as to get superior physical and chemical properties and also to follow the
progress in the manufacturing process, such as conventional casting, directionally solidification
and single crystal growth.

We have been developing a d-electrons concept for the theoretical design of nickel-
based superalloys. This concept is based on DV-Xα molecular orbital calculations of the
electronic structures of Ni alloys. In this concept two electronic parameters are utilized for
treating the alloying behaviour in a quantitative way. One is the bond order, Bo, between the
alloying element and the nickel atom, and the other is the d-orbital energy level, Md, of the
alloying element. Both of these parameters change periodically with the position of the
elements in the periodic table. In other words, the knowledge of the periodic table of the
elements (e.g., electronegativity, atomic size and chemical bond strength) is well condensed
in these two electronic parameters. The compositional average of these parameters are
defined as $\overline{Bo}$ and $\overline{Md}$.

The purposes of this study are to show the evolution process of superalloys by using
these parameters and to present a guide map for the future alloy design and development. In
the $\overline{Bo}$-$\overline{Md}$ map, a third generation superalloy, Rene N6, is located near the second generation
superalloys such as PWA1484, Rene N5 and CMSX-4. Compared to these alloys, the first
generation superalloys including CMSX-11B and -11C, are located in the higher $\overline{Bo}$ and
higher $\overline{Md}$ region. Thus, the evolution of nickel-based superalloys so far developed in the
world are traceable readily using these two electronic parameters.
CRSS-ANISOTROPY AND TENSION-COMPRESSION ASYMMETRY OF A NICKEL-BASE SUPERALLOY

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Abstract
The mechanical behaviour of the chromium-rich monocrystalline nickel-base superalloy SC16 was analysed on the basis of slip systems and dislocation structures. Tensile and compression tests were performed at a strain rate of $10^{-3}$ s$^{-1}$ in the temperature range 650°C - 850°C with five orientations distributed evenly over the stereographic standard triangle. The critical resolved shear stress (CRSS) on the primary octahedral slip system varied systematically with crystal orientation, suggesting that Schmid’s law is not valid in its original form. An extended Schmid law was applied, enabling the description of CRSS-anisotropy and tension-compression asymmetry.
ESTIMATION OF CREEP RUPTURE STRENGTH
IN NICKEL BASE SUPERALLOYS

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Abstract
The creep rupture life of nickel base superalloys has been modelled using a neural network model within a Bayesian framework. A 'committee' model was also introduced to increase the accuracy of the predictions. The rupture life was modelled as a function of 42 variables, including temperature, chemical composition: Cr, Co, C, Si, Mn, P, S, Mo, Cu, Ti, Al, B, N, Nb, Ta, Zr, Fe, W, V, Hf, Re, Mg, ThO₂, La, four steps of heat treatment (each characterised by temperature, duration and cooling rate), sample shape, solidification method. The Bayesian method puts error bars on the predicted value of the rupture strength and allows the significance of each individual factor to be estimated. The magnitude of the error bar can vary with the location in the input space, depending on the perceived level of noise in the data and on the error in fitting data. This enables the model to be used with greater confidence.

Keywords: creep rupture strength, neural network, Bayesian inference, nickel-base superalloys
LIFE ASSESSMENT TECHNIQUES FOR
GAS TURBINE HOT-SECTION COMPONENTS

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Abstract
To extend the components life and inspection intervals, life assessment program of hot section components in gas turbines has started internally since 1986. The first step was to evaluate the conditions of actual components at the periodic inspections nondestructively and destructively and then to determine the life-limited factors in each component. According to the results, we developed three kinds of technologies, which are metallurgical assessment to evaluate the material degradation from microstructure changes, damage assessment to evaluate trends of the cracking, wear and deflection during operations, and simulation analyses to predict the components conditions in the different operating modes. Those techniques are now still under development for each component, such as combustion liners, transition pieces, buckets, and nozzles, and some of the methods developed are now being applied to assess the actual components life.
Large scale numerical simulation of particle coarsening in elastically stressed solids

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Abstract

Large scale numerical simulations of particle coarsening in an elastically anisotropic system are performed. We model Ni based superalloys where the second phase particles have the lattice constant different from that of the matrix. The excess energy of the system is given by a sum of the interfacial and elastic energies. The interfaces move by the flow of mass through the matrix in order to reduce the excess energy. We employ very efficient computational methods which enable us to use very large systems. The simulations are started using circular particles randomly placed in a computational cell. The particles change their shapes from circles to four-fold symmetric shapes to two-fold symmetric shapes during coarsening. In addition, the particles tend to align along $<100>$ directions due to the configurational forces generated by other particles.

Keywords: microstructural evolution, diffusion, elasticity.
MICROSTRUCTURALLY BASED DETERMINATION OF THE LOCALLY ACTING SERVICE TEMPERATURE AND STRESS IN A TURBINE BLADE AFTER SERVICE

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Abstract

During service of a turbine blade the microstructure of the nickel-base superalloys transforms into a plate-like raft structure, which is well-known from tensile creep tests. In addition, anisotropic changes of the lattice parameters ($a_\gamma$ and $a'_\gamma$) of the phases $\gamma$ and $\gamma'$ and of the lattice misfit $\delta$ are found. Quantitative evaluation of dislocation networks on the $\gamma/\gamma'$- interfaces by transmission electron microscopy (TEM) and the analysis of X-ray peak profiles are used for the characterization of the local values of $\delta$ at critical sites of the blade. It can be shown that these values are characteristic for a given deformation temperature and the deformation stress. A comparison of the data obtained from the turbine blade with the evaluated lattice misfits from a set of tensile creep tests permits a retrospective evaluation of the directions and the magnitudes of the stresses and the temperatures that had prevailed locally.
Life Extension of Superalloy Disks by Prevention of Stress Accelerated Grain Boundary Oxidation

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Abstract
The elevated temperature crack growth resistance of Ni-base disk is of importance for gas turbine applications and prospective ultra high temperature steam turbine processes. Wrought Ni-base superalloys such as INCONEL 706 and INCONEL 718 are currently limited to service temperatures of about 600°C-650°C partly because stress accelerated grain boundary oxidation (SAGBO) causes exceedingly high crack propagation rates at elevated temperatures. In the past, a number of techniques such as heat treatment modification [1], grain coarsening [2] or manufacturing of dual alloy disks [3] have been established to counter this effect. Unfortunately, these techniques adversely affect other important properties such as yield strength, sonic inspectability or manufacturing costs. Recently, an alternative approach has been developed [4,5] which utilizes a boron concentration gradient to protect the component surface against environmental embrittlement. In this paper the effect of this treatment on static and cyclic properties is discussed. It is shown that significant life extension at elevated temperatures is attained due to this novel approach.

Keywords: Boronizing, Wrought Alloys, Inconel 706, SAGBO
INTEGRITY ASSESSMENT OF HVOF REPAIRED INDUSTRIAL GAS TURBINE VANES

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Abstract

High Velocity Oxi Fuel (HVOF) was used as a reparation technique for test samples of Co-base alloy typically used for gas turbine hot path components. Phase composition and surface residual stress were studied by X-ray Diffraction, whereas interface adhesion defects were imaged as ‘hot spots’ by Video Pulsed Thermography. The X-ray Residual Stress Analysis gave a direct evidence of the effectiveness of a post-deposition heat treatment in relieving the surface tensile stress produced during the HVOF spraying.
FRECKLE FORMATION IN LARGE SUPERALLOY
SINGLE CRYSTAL AIRFOIL CASTINGS

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Abstract
Freckles are presently one of the main defects encountered in advanced casting technology of superalloys. The evaluation of a numerical criterion able to provide quantitative insight on freckling conditions is now recognized as a major key toward the successful manufacture of large SX castings. The Rayleigh criterion seems best adapted to freckling prediction but cannot currently explain why freckles form only at the surface of SX castings. It is suggested that the angle of the solidification front plays a critical role on freckle formation. An experimental Bridgman-type furnace was built in order to directionally solidify freckle-prone superalloys (Waspaloy and Mar-M247) at various angles to the vertical direction, under typical industrial conditions (5<\(C<40^\circ\)C/cm and 1<\(R<6\)mm/min). Evaluation of the solidification conditions was done by numerical modeling. A “modified Rayleigh criterion” is suggested and is shown to describe more accurately the effect of the casting conditions and growth front angle on freckling.
Advanced Repair Techniques for Modern Industrial Gas Turbines

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Abstract
Improved welding and brazing processes have been applied to the repair of industrial gas turbine blade tips. Blade tip repair by TIG welding at elevated temperatures (SWIP® process) shows that even the new generation of cast superalloys such as directionally solidified (DS) and single crystal (SC) alloys can be welded without crack formation in the heat affected zone (HAZ). Thermochemical cleaning and subsequent diffusion brazing has been evaluated for the crack repair of conventionally cast vanes as well as for TMF specimens cast in DS and SC alloys. The results show that after optimizing the brazing process, both the microstructural and mechanical properties of brazed joints meet the material requirements.

Keywords: Repair, Welding, Brazing, Directionally Solidified and Single Crystalline Alloys

1 Introduction

Modern industrial gas turbine blade tips have to withstand higher gas temperatures (T > 1400°C) due to the increasing thermal efficiencies (up to 60% in combined cycle). This requires improvement by introducing improved cooling techniques together with thermal barrier coatings and new blade materials such as directionally solidified (DS) and single crystal (SC) alloys. However, the additional requests for low maintenance costs and guaranteed material life times have become critical issues, since most of the currently used reconditioning and repair techniques can not be applied to the new types of blade tips. The increasing complexity of their shapes (thin wall sections, large number of cooling holes) and the difficulty to repair DS and SX alloys require the implementation of advanced repair processes.

Since improved welding and brazing processes have already been established in the aerospace maintenance business, it has become an increasing interest to transfer such techniques to the repair of industrial gas turbine components. Different attempts have been made in order to overcome the cracking problems during welding; either a controlled and limited heat input is used (e.g. by laser beam welding, electron beam welding and microplasma welding [1]), or, the workpiece is preheated during TIG welding in order to reduce continuously stresses that arise during welding [2]. In a recent work, epitaxial laser metal forming has been presented as a potential technique for single crystal repair [3]. Brazing which is an important repair process for turbine vanes, has been significantly improved in terms of crack repair due to more efficient cleaning procedures and optimized brazing cycles. Acceptable ductility of the brazed joints has been achieved [4].

In this paper, the evaluation of two improved repair processes, i.e. the blade tip repair by TIG welding at elevated temperatures and the crack repair by thermochemical cleaning followed by high temperature brazing, is presented. Both techniques have been applied to the repair of different blading materials (IN738LC, DS CM247LC, CMSX-4). In the course of process certification, metallurgical investigations as well as mechanical testings were undertaken.
Single Crystal Turbine Components Repaired by Epitaxial Laser Metal Forming

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Abstract

Epitaxial laser metal forming (E-LMF) is presented as a new technique to repair and reshape single crystal gas turbine components. E-LMF consists of impinging a jet of metallic powder onto a molten pool formed by controlled laser heating. Laser surface treatment has the advantage that heat input is very localized, thus leading to large temperature gradients (typically around 10^6 K/m). This is used, in unison with closely controlled solidification velocities, to stabilize the columnar dendritic growth, thereby avoiding the nucleation and growth of equiaxed grains in the laser clad. E-LMF, therefore, is an ideal technique to deposit single crystal laser clads by epitaxial growth onto a single crystal. The microstructure is analyzed by indexing the electron backscattered diffraction patterns (EBSD). Applications of E-LMF to turbine blade reshaping is presented.

Keywords: Repair, Laser Cladding, Single Crystal Turbine Blade, Epitaxy
EFFECT OF Ti ADDITIONS ON ISOTHERMAL AND CYCLIC OXIDATION OF NiCrAlY COATING ALLOYS FOR GAS TURBINE APPLICATION

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Abstract
Model alloys with compositions (Ni-20Cr-10Al-0.4Y) similar to commercial coating compositions were investigated with respect to the question whether and how Ti additions up to 2% affect the protective properties of the alumina surface scale. The isothermal and cyclic oxidation tests were carried out in air and Ar/O2. The specimens were examined by optical metallography, SEM/EDX, TEM, SNMS and dilatometry. It was found that Ti strongly affects the alloy phase composition and microstructure rather than changing the growth mechanisms of the oxide scale. The resulting change in alloy thermal expansion coefficient by the presence of Ti appeared to have a significant effect on alumina scale adherence.
Annealing of NiCr- and Ni-superalloy interfaces

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Specimens were prepared by atmospheric plasma spraying. Two types of coating were used, namely pure Ni and Ni20Cr; substrates were Ni based superalloys single crystals SC 16 and CMSX-4. The structure of specimens annealed at temperatures 850 - 1050 °C was evaluated using optical metallography, microhardness measurement, scanning electron microscopy and EDS microanalysis.

The results show that substantial changes of structure take place in the substrate region adjacent to the coating. The extent of the region affected by diffusion between coating and substrate depends on the annealing temperature and time, and also on the coating and substrate composition.

The first structure modifications involve gradual dissolution of ordered Ni3Al phase and simultaneous coarsening of remaining Ni3Al particles (their elongation in direction perpendicular to the interface). Aluminium and titanium (if present) released by this process diffuse toward the coating or free surface. Ti is moving faster than Al. At lower temperatures, no significant amount of oxygen was found in Al and Ti rich layer. The specimens annealed with Ti chips were infiltrated from free surface by Ti.

At 1050 °C, both coating - substrate interface and free surface accommodate oxide layers. At free surface, outer Ti oxide layer is separated from Al oxide region by disordered γ solid solution region.

When annealing time is sufficient, chromium and molybdenum form elongated particles inside the γ solid solution after complete dissolution of Ni3Al phase.

If chromium is present in the coating, above described structural modifications are retarded. This was also confirmed by annealing couples formed by the same coatings on the pure Al substrate. In this case, Cr presence slows down diffusion of Ni into Al substrate. Mixed layer with composition of intermetallic phase constitutes. Its nanostructure character was proved by transmission and electron microscopy and diffraction.

Structure analysis showed that high affinity of Al and Ti to nickel and eventually to oxygen leads to the destruction of the superalloy structure in the vicinity of coating or free surface. At highest temperature (1050 °C) oxide layers grow on the free surface and at the coating - substrate interface.

Diffusion in the interface vicinity lead to the voids formation in the coating adjacent to the interface.
ISOTHERMAL OXIDATION BEHAVIOUR OF PLATINUM MODIFIED ALUMINIDE DIFFUSION COATINGS ON A SINGLE CRYSTAL NICKEL BASED SUPERALLOY

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Abstract
Two different Pt modified Al diffusion coatings (SS82A and MDC150L), on a single crystal Ni base superalloy (CMSX4), have been oxidised for 50 and 100 h at 1050 °C in laboratory air. The microstructural changes of the coating layers were investigated before and after oxidation tests by means of Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Both coatings produced continuous oxide scales with a thickness of approximately 1 µm. It was found that the thickness of the SS82A coating increased quite rapidly, while the thickness of the MDC150L coating remained fairly constant. The interdiffusion layer of the SS82A coating contained small, equiaxed grains, that besides Ni, were rich in W, Co and Cr. In the corresponding layer in MDC150L, a phase with similar composition was present, but it showed a clearly columnar structure. Changes in elemental distribution through the coatings were measured.

Keywords: nickel base superalloy, PtAl diffusion coating, platinum, high temperature oxidation
HIGH TEMPERATURE RESISTANT MeCrAlY+Al COATINGS OBTAINED BY THE Arc-PVD METHOD ON Ni BASE SUPERALLOYS

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Abstract

Investigations of obtaining high temperature coatings on the Ni base superalloys by the Arc-PVD method, using exothermic reaction processes between Ni and Al with NiAl intermetallic formation are presented in the article. By the diffusion heating at 1050°C NiAl high temperature diffusion coating containing 21 % at. Al and 50 μm thick was obtained. In the next stage coatings with more complex chemical composition - NiCoCrAlY were formed. The NiCoCrAlY coatings were made of two targets good consistence between the chemical composition of the targets of the coatings and an uniform distribution of elements in the coatings were shown. Then the surface was covered with aluminium also by the Arc-PVD method. In the vacuum chamber of the equipment a synthesis reaction between NiCoCrAlY and Al with the formation of NiAl intermetallics of high Co, Cr, Y content was initiated. The final heat treatment of coatings was conducted in the air and vacuum at 1050°C. The strong segregation of yttrium in to the oxide scale in the specimens heated in the air was shown. It was possible to obtain NiAl intermetallics phase coatings modified by Co, Cr and Y by the Arc-PVD method. An example of the application of this method for the aircraft engine turbine blades was presented.

Keywords: High temperature corrosion, MeCrAlY coatings, Arc-PVD method.
Metallurgical Temperature Estimates Based on Interdiffusion Between CoCrAlY Overlay Coatings and a Directionally Solidified Nickel-Base Superalloy Substrate

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Abstract
The interdiffusion reactions between vacuum plasma sprayed (VPS) and over-aluminized VPS CoCrAlY coatings, GT-29 and GT-29 In-Plus, and a directionally solidified nickel-base superalloy, DS GTD-111, were characterized and used to estimate the operating temperatures of service-exposed combustion turbine buckets. The interdiffusion zone growth kinetics were measured and the temperature dependence of the interdiffusion rate constants determined. A model was developed to estimate surface temperatures based on the observed and calibrated rates of coating/substrate interdiffusion. The model was applied in the analysis of service-exposed GE MS7001F first stage turbine buckets. Metallurgical temperature estimates obtained from the coating / base metal interdiffusion model were in reasonable agreement with those obtained independently from an analysis of gamma prime precipitate coarsening and infrared pyrometry data.
MICROSTRUCTURE AND HOT CORROSION BEHAVIOR OF Pt-AL COATINGS ON IN738 NICKEL-BASE SUPERALLOY

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Abstract

An investigation has been carried out to study the Na$_2$SO$_4$ and Na$_2$SO$_4$ + NaCl induced hot corrosion of Pt-modified aluminide coatings on a nickel-base superalloy IN738 at 900°C in air. The corrosion resistance of Pt-Al coating is dependent on its structure features. The coating with a continuous PtAl$_2$ surface layer appears less corrosion-resistant than that with PtAl$_2$ + NiAl two phases. The addition of NaCl into Na$_2$SO$_4$ considerably accelerates the degradation of Pt-Al coatings, causing the coatings to suffer severe internal oxidation and sulfidation. It is worthwhile to note that the internal oxidation and sulfidation of the intermediate coating layer are heavier than that of the outer layer. Because of the volume expansion of these internal oxides and sulfides, microcracks appear between the outer and intermediate layer. These cracks develop quickly and cause the outer layer spalling.

Keywords: Superalloy, Pt-Al Coating, Hot Corrosion,
High Temperature Corrosion Resistance of Gas Turbine Materials and Coatings under the Influence of Cl-Contaminations

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Abstract
Depending on fuel and service environment combustion atmospheres of gas turbines may contain contaminations of Cl-species. There has been some uncertainty on how such small Cl-impurities affect the behaviour of the protective oxide scales. In the work reported, therefore, tests under isothermal and thermal cyclic conditions were performed at 1000°C in air containing 100 ppm HCl. The materials were CM247LC DS and IN792DS as bulk materials and CM247LC DS with two types of overlay CoNiCrAl coatings where one was free of Y while the other one contained about 0.5% Y. The results showed that there can be a significant influence of such small impurities on oxide scale adhesion and the course of materials damage and that also in this case a key role is played by Y-additions in the coating if Cl-impurities are present in the environment.
CREEP OF COATED AND UNCOATED THIN-SECTION CMSX-4

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Abstract
Creep testing has been carried out on coated and uncoated specimens of the single crystal nickel-base superalloy CMSX-4 at 850 and 950°C. The test pieces were hollow with a <001> orientation. Some specimens were coated with a Pt-Al coating on the outside and a plain aluminide coating on the inner bore, other specimens were left uncoated. Coated and uncoated specimens exhibited similar creep rates but the elongations and lives of the coated specimens were reduced slightly at 950°C and long testing times. Creep failure occurred by the growth and linkage of cracks initiated at casting porosity in the interdendritic regions. Oxidation effects were much less at 850°C than at 950°C for both coatings. The platinum-aluminide had better corrosion resistance and slightly greater ductility. Taking into account the reduction in load bearing area caused by the coatings, the difference in creep behaviour of the coated and uncoated specimens was marginal, as shown by the application of the Larson-Miller parameter.

Keywords: creep, single crystal superalloy, coating, thin section
LOW-CYCLE AND THERMO-MECHANICAL FATIGUE OF COATED IN738LC

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ABSTRACT
The objective of this study was to investigate the effect of coatings on thermo-mechanical fatigue (TMF) behavior of IN738LC for turbine blading. In-phase and out-of-phase TMF tests at 400°C-850°C and isothermal low-cycle fatigue (LCF) tests at 400°C and 850°C have been performed in both a CoCrAlY-coated and uncoated conditions by an improved test system. Tensile tests of the CoCrAlY-coating at several temperatures were also performed in order to understand the mechanical properties of the coating. The crack initiation sites and the crack propagation paths of specimens were also analyzed by SEM after testing. The life of in-phase TMF were coincident to the life of LCF at 850°C and the behavior was similar both in coated and uncoated conditions. However, the quite different behavior between out-of-phase TMF and LCF lives of coated specimens were obtained. The main reason consists in the crack initiation site and the mechanical behavior of the coating.

Keywords: Thermo-mechanical fatigue, Low-cycle fatigue, IN738LC, Coating
Nondestructive Integrity Characterisation And Assessment Of Gas Turbine Coatings Within The COST-501 Program

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Abstract
Different NDT-techniques are presented with respect to the evaluation of metallic and ceramic coatings. Multi-frequency eddy current testing has been applied successfully to collect data on coating thickness of NiCoCrAlY layers. Pulsed video thermography is shown to yield data on coating thickness as well as on the existence of bonding defects between layer and substrate. X-Ray diffraction analysis could be applied to gain information on stress states, phase compositions of materials and texture. High frequency ultrasonic testing has been used to detect bonding defects between ceramic coating and substrate material. Thermal wave analysis, an advanced testing technique, has been used for the determination of coating thickness homogeneity; these results will have to be verified by metallographical investigations.
FAILURE MECHANISMS IN THERMAL CYCLED TBC'S

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Abstract. Multilayered coatings are increasingly being used in several technological applications, such as thermal protection of engine components. This contribution discusses the role of thermal stresses on the thermo-mechanical integrity of protective ceramic coatings for use at high temperature, such as thermal barrier coatings. Modelling of thermal residual stresses in multilayered and graded coatings is presented. This modelling enables us to calculate the transient thermal strains and stresses by an elasto-plastic biaxial stress model which contribute to a better understanding of the failure modes in TBC's tested at high temperatures (furnace cycling and rapid thermal cycling). The TBC failure mechanisms are discussed in the light of coating transient stresses, interfacial oxidation, rugosity at interfaces and cohesive strength of the individual layers in the TBC system.
INNOVATIVE PLASMA SPRAYED 7%YSZ - THERMAL BARRIER COATINGS FOR GAS TURBINES

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In the last years high performance Yttria-Stabilised Zirconia Thermal Barrier Coatings (TBCs) were industrially applied on vanes and blades of gas turbines engines by the Electron Beam Physical Vapour Deposition (EB-PVD) technology. Their high Thermal Shock Resistance have often been correlated to the stable microstructure, which consists of vertically-oriented grains, strongly bonded to the substrate, but weakly connected to each other: a microstructure tolerant to tensile strain i.e. stresses, is therefore obtained parallel to the surface.

Unfortunately, the EB-PVD process is characterised by high costs and EB-PVD TBCs ensure a thermal protection which is half of that of Plasma Sprayed TBCs, for the same ceramic thickness. Therefore efforts are still in course to verify the possibility to improve Plasma Sprayed technology.

The activity of COST 501-III, WP15 on TBCs was concentrated on the testing of spray technologies alternative to the standard Air Plasma Spraying (APS), to reach a higher TBCs strain tolerance, through a higher porosity or a vertical segmentation.

The aim of this paper is to review the manufacturing techniques developed by the different COST partners and to present preliminary TBCs characterisations.

The vertical segmentation was achieved by a special APS, by Low Pressure Plasma Spraying (LPPS), at high temperatures, and by the use of a cryogenic cooling. Very porous TBCs were manufactured by low power APS. Finally the effect of the pressure on TBC manufacturing was investigated between 1200 and 3000 mbar by High Pressure Plasma Spraying (HPSP).

Preliminary results indicate that the improvement of the microstructure of plasma sprayed TBC i.e. of their Thermal Shock Resistance, is possible.

A foreseen prosecution of the current co-operation will include thermal shock tests between 7wt%YSZ-TBCs manufactured by all these different spray techniques and the EB-PVD TBC.
RESIDUAL STRESSES IN HIGH TEMPERATURE MULTILAYERED COATINGS FOR ADVANCED POWER ENGINEERING

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Abstract: Yttria stabilized zirconia plasma sprayed coatings (PS top coating) were applied on high temperature Ni based alloys precoated with a thin, dense stabilized zirconia coating produced by Physical Vapour Deposition (PVD bond coating). The coating residual stress was studied experimentally (by X-ray Diffraction, MicroRaman techniques and by microdisplacement laser transducer) and numerically in the thermal barrier multilayered system for the as-deposited coatings and after different thermal cycling processes. The PVD bond coating has an in-plane compressive residual stress after deposition (about -320 MPa). The plasma sprayed top coating has a compressive stress near the interface and presents low tensile (or compressive) stress at the surface after the plasma spraying deposition (-20 MPa to 30 MPa depending on the substrate temperature and coating thickness). After thermal cycling the stress changes to -760 MPa for the PVD bond coat and the PS coating stress changes to a compressive value of about -280 MPa. The stress within Cr2O3 scale was -1680 MPa as determined by MicroRaman spectroscopy. The residual stresses within the TBC during thermal cycling were modelled and the numerical results are in good agreement with the experimental measurements.
New materials for advanced thermal barrier coatings

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Abstract
New ceramic materials are investigated with respect to an application as thermal barrier coatings. Important criteria for the selection of the materials are low thermal conductivity and high melting points. In this investigation composite materials based on zirconia and ceria are included. The effect of non-soluble dispersions in the ceramic matrix on the sintering behaviour and on thermomechanical properties is discussed. Furthermore plasma sprayed coatings are produced and characterized. Amounts of 20 wt% of a second phase with a lower melting point than the matrix compound lead to a considerable increase of coating density and consequently an optimization of the spray process is necessary. Besides the CeO$_2$- and ZrO$_2$-based composites new oxide ceramic materials with high melting points have been investigated. For these materials relevant thermomechanical data are missing. Therefore bulk materials have been synthesized and characterized. Low sintering activity of the materials was observed. The measured thermomechanical properties are compared with yttria-stabilized zirconia materials.

Keywords: new thermal barrier coatings, sintering activity, thermal conductivity, coefficient of thermal expansion, zirconate.
Burner Rig Tests of EB-PVD Thermal Barrier Coatings under Hot Corrosion Conditions

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Abstract

Thermal barrier coatings (TBCs) deposited by electron beam - physical vapor deposition (EB-PVD) were cyclically tested at 900 °C under hot corrosion conditions in a high-velocity burner rig for 100 and 200 h. The TBC system on the Ni-base superalloy MarM002 consisted of an approximately 100 μm thick EB-PVD NiCoCrAlY bond coat and a 200-300 μm thick top coat of zirconia partially stabilized with 7 wt% yttria (PYSZ). Mass change of the test specimens was measured and the degradation of the ceramic top coating as well as the oxidation attack of the bond coat was metallographically examined. Cracking and spalling of the PYSZ coating was investigated by the scanning electron microscopy. Hot corrosion attack, which normally occurs on metallic high temperature materials due to the effects of molten salt deposits such as sodium sulphate, was not found on PYSZ coatings. The failure of the TBCs mainly resulted from cracking within the zirconia columns and concurrent loss of material hereby significantly roughening the surface. This failure mode seems to be caused by mechanical erosion. A second failure mode was due to the presence of growth defects formed during the PVD process. Test conditions caused spallation of these defects, resulting in pitting on the surface.

Keywords: thermal barrier coatings, burner rig tests, hot corrosion, erosion
Residual Stresses in Zirconia Thermal Barrier Coatings due to Strongly Inhomogeneous Temperature Distributions

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Abstract
Residual stresses have been analyzed in a duplex thermal barrier coating consisting of a plasma sprayed ceramic layer of 7wt%Y₂O₃ stabilized zirconia and a low pressure plasma sprayed MCrAIY bond layer both deposited on an In718 substrate. To simulate realistic thermal conditions, a sample environment in form of a gradient furnace has been developed to achieve well defined temperature gradients across the thickness of the specimen. The investigations of the thermal stresses have been performed in-situ under different thermal loads with diffraction methods. The stress state of the thermal barrier coating was found to depend strongly on the temperature distribution across the sample. The influence of both, the different thermal expansion coefficients and the temperature gradient across the thickness of the specimen on the residual stress state are discussed with regard to the fatigue behaviour of this thermal barrier coating system.

Keywords: thermal barrier coatings, inhomogeneous temperature distribution, in-situ stress analysis
Microstructure and Modelling of coated Superalloys

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Abstract
In the present study the hot deformation behaviour and the microstructure development of uncoated and TBC-coated superalloys NiCr22Co12Mo9 and CoCr22Ni22W14 has been investigated at temperatures between 750 and 950 °C. Estimating parameters like dislocation density and carbide spacing the hot tension, creep and relaxation behaviour has been connected with the microstructure. A TBC-coating of the sheet materials by plasma spraying lead to a decrease of the creep resistance and to a shorter creep life time. The worsening of the mechanical properties results from the degradation of the solid solution and the carbide precipitation hardening in the interface region.
In order to predict the deformation behaviour of the superalloys, the estimated microstructure parameters have been used as input data for an effective stress model and a modified Kocks-Mecking model, which describe the high temperature deformation. The simulation yields to correct predictions of the creep, tensile and the relaxation behaviour of the superalloys.
Finite element analysis of thermal stresses in thermal barrier coatings on cylindrical substrates

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Abstract
Spallation of thermal barrier coatings (TBCs) in gas turbines often occurs at the ends of the blades, where radii of curvature are very small. This failure might be due to tensile stress components perpendicular to the interface and due to circumferential tensile stress components in convex curved layered systems. A finite element method (ABAQUS) is used to calculate stress development during a thermal cycle. The influence of the radii of the interface and the coating thicknesses on these stresses are investigated. The investigated system consists of a cylindrical substrate (Ni-base-superalloy), a bondcoat (CoCrAlY) and the TBC (ZrO$_2$+7%Y$_2$O$_3$). The viscoelastic properties of the materials are taken into account. Especially the bondcoat creeps readily at temperatures above 700°C. This leads to a stress-relaxation of the specimens. The results of numerical calculations are compared to values obtained by an analytical elastic model. An analytical formulation of the influence of curvature and coating thickness on the stresses is expected to be helpful for the elaboration of a life time model for TBCs.
NUMERICAL SOLUTION OF INVERSE PROBLEM FOR DIFFUSION AND CORROSION PROCESSES IN MATERIALS FOR GAS TURBINE

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Modeling of high-temperature corrosion and diffusion in materials for gas turbine are important for engineering and industry. To make corrosion and diffusion predictions for a long time by means of mathematical model seems to be possible only if rather exact model's coefficients are on hand. The aims of this paper are inverse problem methodical development and its application to determine parameters of diffusion and corrosion mathematical model by means of inverse problem solution using the data of laboratory testing. The approach allows to predict the diffusion and corrosion processes of gas turbine blade materials at the high temperature. This approach is based on effective modern methods of parameter identification of diffusion and oxidation models using experimental data. To determine the unknown parameters the procedure of the iterative identification has been applied, which was based on Gauss-Newton's technique. The parametrical sensitivity analysis of the calculated characteristics at the measurement points (concentration distribution and oxidation depth of alloys treated at high temperature) to variation in the desired parameters (coefficients of mass transfer, diffusion, etc.) was carried. The results of inverse test problems solution both for exact an unexact input measurement values concentration of alloying elements and oxidation depth are given in the paper.
LIFE TIME MODELING FOR MCRAIY COATINGS OF GAS TURBINE BLADES.

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The life time of gas turbine blades is mainly controlled by oxidation resistance of coatings. The development of mathematical model of high temperature oxidation and diffusion and life time modeling are purposes of this paper.

The mathematical model of diffusion and oxidation is described by diffusion equations of alloying elements and oxidant with oxidation processes taking into consideration by mass source term. The diffusion and oxidation mathematical model is integrated by numerical methods (the finite difference method). It permits one to take into consideration the most general peculiarities of the problem formulation: - the multilayer, the relationships between coefficients and coordinate, time and concentration.

For determination of model key parameters (diffusion, mass transfer, mass uptaking coefficients, etc.) the inverse problem solutions were used.

Both elements concentrate distribution and oxide thickness were calculated using determined coefficients for experimental data. The experimental data and calculated results of concentration distribution are in good correspondence.

The usage of model and determined by inverse problem solution model parameters allowed to do the lifetime modeling of the diffusion and oxidation alloy with and without metal-ceramic coatings at the high temperatures and long term duration.

Keywords: life time, modelling, diffusion, oxidation, gas turbine, blade
ASSESSMENT OF TURBINE HOT GAS PATH COMPONENTS

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Abstract
In recent years experience has accumulated on different methods for life-assessment of components of hot gas paths in gas turbines. In this report attention is focused on buckets and nozzles of turbines designed by Nuovo Pignone SpA. Buckets are currently made of different Ni-base superalloys. From design data, the distribution of temperatures on bucket sections can be calculated. The actual metal temperatures of serviced buckets can instead be assessed by metallographic observation. The evolution of the $\gamma'$ phase has been used for effecting a quantitative evaluation of the service temperature at each location on the bucket. The kinetics of $\gamma'$ phase evolution is similar among the various Ni-base superalloys, but for accurate temperature estimation, each alloy requires a study of its own.

As soon as the actual metal temperature has been estimated, it becomes possible to evaluate the residual life by applying different damage models. FEM thermal and mechanical analyses are re-run to match the temperature distribution estimated from metallographic examination.

Nozzles are usually made of Co-base superalloys of which FSX 414 is the most widely used. Co-base superalloys are strengthened mainly by the presence of carbide second phases. The modifications observed in the morphology and composition of carbides can be used to assess service temperature and damage evolution. Image analysis using backscattered electrons is considered to be a sensitive tool. Feasibility studies have shown that the method is capable of estimating the exposure at different temperatures of FSX 414. Research is now under way to transfer this evaluation to a quantitative level. Experimental research combined with continuous monitoring of the machine will make it possible to set up quantitative methods for assessing service temperature and material degradation of FSX414 components.
AN INFLUENCE OF THE STRUCTURE OF THE THERMAL BARRIER COATINGS ON THERMAL SHOCK AND CORROSION RESISTANCE

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Abstract
Results of investigations on obtaining the thermal barrier coatings (TBC) and their properties have been presented in the article. Coatings were formed by a thermal spraying method using a A3000 system controlled by computer and with the ABB robot. For spraying the following materials: ZrO$_2$Y$_2$O$_3$ - Metco 204 B-NS and MeCrAlY - Amdry 962 as an interlayer were used. The coating structure examinations were made. Powder morphology was determined by the scanning microscope method. Tests by the thermal shock method were conducted in the air atmosphere by heating the specimens to 1200°C for 15 min. and cooling to 250°C for 5 min. The best results were obtained at the ceramic coatings thickness of 0.2-0.3 mm and the transient coating of 0.1-0.15 mm. The comparative analysis showed low resistance to thermal shocks of MeCrAlY +Al$_2$O$_3$ coatings. Hot corrosion resistance tests were conducted at 900°C in the Na$_2$SO$_4$ medium. Tests showed low resistance of TBC coatings to that type of corrosion. The TBC coatings were formed on the aircraft combustion chamber.

Keywords: TBC coatings, high temperature corrosion, plasma spraying.
THE SURFACE STRUCTURE OF GAS TURBINE BLADES

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Abstract
The X-ray analysis method has been used to study the phase structure of gas turbine blades in operation. The structure and composition of oxide, sulfide and sulfate phases as well as the structure of oxides on electron-beam MCrAlY coated surfaces have been established for fixed and rotor nickel-base alloy blades after service. The phase state of matrix solid solution of the coating in different blade areas after service has been investigated.

Keywords: blade, surface, operation, phase composition
HEAT TREATMENT OF GAS TURBINE BLADES
WITH PROTECTIVE COATINGS.

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Abstract
The revealed laws of formation of microstructure and features of influence of structure on properties of Ni-base superalloys have allowed to develop bases of a choice of modes of thermal processing blades with coatings at three stages: thermal processing blades before deposition of a coatings, diffusive annealing (reception, carried out practically at all ways, of a coatings) and finishing or reducing of thermal processing ensuring as reception of structure and properties of the basic metal at a level, achievable ambassador of heat treatment of preparation blades without of a coatings and creation optimum for operation of structure of a coatings. For a choice of modes of thermal processing at all three stages of heat treatment blades with coatings the superalloys Ni-base are divided into 4 groups distinguished by a degree alloy - by quantity strengthening phase and temperature of solubility strengthening phase.
ELABORATION OF A YSZ POWDER BY SPRAY DRYING FOR THERMAL BARRIER COATINGS ON GAS TURBINE COMPONENTS

R. Ranc, M. Perez, F. Schuster

Paper will be distributed at the meeting.
Poster Presentations

D1 – D6
STRESS RELAXATION IN METALS AND ALLOYS

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Abstract

Stress relaxation is a process developing during the time of spontaneous change of stress in construction elements. It is a question of the residual stress, as so as the stress caused by external loads in fixed deformation conditions. Various questions, related to the study of stress relaxation processes in materials and details of machines are considered in the present study. The report is illustrated by experimental data on the influence of alloying, thermal and thermomechanical treatment on the relaxation resistance of metals and alloys on the basis of iron, nickel, cobalt, zirconium, copper, aluminium, magnesium, moliobdenium and niobium.

Keywords: Stress relaxation, creep, loading, fracture
ON STATISTICAL ASPECTS OF RESISTANCE TO CYCLIC STRAINING AND FRACTURE

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Abstract

Number of questions, connected with accuracy of determination of resistance to cyclic deforming and fracture of steels and alloys characteristics, is considered. Experiments conducted on 10 melting metal indicate expediency to use relative coordinates (stress ranges and plastic deformations, referred to cyclic limit of elasticity and corresponding deformation) for cyclic curve constructions.

We propose the formula for determination of minimum value of deformations ranges for given number of cycles up to fracture. This formula bases on Manson equation, low cyclic fatigue curve for individual melting and values of limit strength and plasticity dispersions of given material.

Keywords: low-cycle fatigue, cyclic deforming curve, statistical method
DISTRIBUTED DATABASE SYSTEM FOR MUTUAL USAGE OF MATERIAL INFORMATION (DATA-FREE-WAY)

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Abstract

A distributed database system named "Data-Free-Way" for mutual usage of material information was developed under the collaboration of National Research Institute for Metals, Japan Atomic Energy Research Institute, and Power Reactor and Nuclear Fuel Development Corporation in order to share fresh and stimulating information as well as accumulated information for the development of advanced materials, for the design of structural components, etc. Then Japan Science and Technology Corporation joined three above-mentioned organizations. In the original pilot system, material information was mutually utilized through the local circuit. Now the system has been made more substantial through the advanced network with high data processing speed and multi-functions by taking advantage of current excellent data communication techniques like the Internet.

This paper will describe the present status of the new system, which is available through the Internet. Furthermore, some trials of attractive/sophisticated utilization of the system will be mentioned.

Keywords: Distributed material database, Internet, Heat resistant alloy, Creep
NEW SOFTWARE TOOLS FOR LIFETIME PREDICTION
OF HIGH TEMPERATURE COMPONENTS
UNDER SERVICE LOADING

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Abstract

Special software tools were developed to assist the industrial specialist in lifetime prediction and supervision of steam power plant components. A programme DESA was developed for the parametric assessment of creep and creep rupture data to obtain either property values for design purposes or basic data for modelling creep behaviour. A programme KARA contains creep equations for several heat resistant steels and superalloys. For finite element application, KARA is available in the form of a user subroutine. Further, a programme LARA is available for life calculations under cyclic creep loading conditions. The modified life fraction rule and a factor concept of the relative creep or rupture life of this rule are the basis of LARA which can be used as a life counter for power plant components.

Keywords: creep rupture data, parametric assessment, creep equations, cyclic creep, life fraction rule
ALKALI RELEASE AND SORPTION IN COAL COMBUSTION

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Abstract
Alkali metals play a key role for the realization and improvement of coal-fired combined cycle plants. Released as gaseous species during coal combustion, alkali metal compounds cause high temperature corrosion especially at the gas turbine blading. This paper presents experimental and theoretical basic investigations, which contribute to the understanding of the release and sorption of these contaminants. Knudsen effusion mass spectrometry was used to study the vaporization of coal ashes and slags at temperatures between 200 and 1800°C and to determine the released alkali species and their partial pressures. The database system FACT and the modified quasi-chemical model for non-ideal solutions were applied to predict the equilibrium state of model systems for coal slags and to determine material compositions for maximum alkali sorption capacity.

Keywords: coal conversion, hot gas cleaning, coal ash, alkali release, alkali sorbents.
This book contains the abstracts of the papers presented at the 6th Liège Conference on Materials for Advanced Power Engineering held from 5 to 7 October 1998 in Liège, Belgium.