

Forschungszentrum Jülich
in der Helmholtz-Gemeinschaft



***Materials and Processes
for Advanced Technology:
Materials for Energy Systems***

edited by
D. Stöver, M. Bram

International Cooperation

Bilateral Seminars

Vol. 33

Forschungszentrum Jülich GmbH
Bilateral Seminars of the International Bureau

Egyptian - German Workshop on

Materials and Processes for Advanced Technology:

Materials for Energy Systems

Cairo 7 - 9 April 2002

edited by
Detlev Stöver, Martin Bram

Schriften des Forschungszentrums Jülich
Bilateral Seminars of the International Bureau

Vol. 33

ISSN 1433-5581 ISBN 3-89336-320-3

Bibliographic information published by Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche
Nationalbibliografie; detailed bibliographic data is available in the
Internet at <<http://dnb.ddb.de>>.

Publisher
and Distributor: Forschungszentrum Jülich GmbH
Central Library
52425 Jülich
Germany
Phone +49 (0) 24 61 61 - 53 68 · Fax +49 (0) 24 61 61 - 6103
e-mail: zb-publikation@fz-juelich.de
Internet: <http://www.fz-juelich.de/zb>

Coverdesign: Grafische Betriebe, Forschungszentrum Jülich GmbH

Printer: Grafische Betriebe, Forschungszentrum Jülich GmbH

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Schriften des Forschungszentrums Jülich
Bilateral Seminars of the International Bureau Vol. 33

ISSN 1433-5581
ISBN 3-89336-320-3

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Introductory remarks
Prof. Dr. Detlev Stöver

**Joint Egyptian-German Workshop on Materials and Processes for Advanced
Technologies: Materials in Energy Systems**

Excellency

Mrs. Chairman of AEA Prof. Feyza

Dear Colleagues, ladies and gentlemen

It's a great pleasure for me to give you a heartily welcome on behalf of the German delegation. We came here to meet you and celebrate this workshop on materials in energy systems. In parallel I welcome all the participants from Egypt, excellencies, chairmen, professors, scientists, good friends from recent and former times. I welcome as well all the participants of the German delegation, coming from Research Center Jülich but also from R.C. Geesthacht, from Aachen University as well as Siemens industry.

The Egyptian-German cooperation in the field of material research has a long tradition of more than 30 years. (Though it is risky to talk about 30 years tradition in a country where history is counted in milleniums rather than in decades.) Nevertheless this short period of 30 years is about one generation which means that people change maintaining the cooperation. This indeed is happening and coincidently the content of the cooperation has changed from the nuclear business to nowadays nonnuclear items in energy technology. I think materials R+D is really a key point to all substantial advances in existing energy converting systems as well as for the development of really new systems.

New materials and related technologies always create the basis for new processes or often even are the key problems to be solved before technological processes envisaged can be made running. Let's take the fuel cell as an example. The principle of the fuel cell has been discovered in 1839 by Sir William Grove and the famous solid electrolyte which until today is doped zirconia has been discovered in 1899. Nevertheless it took another century to make a solid oxide fuel cell ready for the beginning of a market penetration phase where we are faced with nowadays. And this has been made possible by intensive work on materials and material technology R+D. So in my view we are completely right to

rely on and deal with materials in energy technology and to care especially about cooperation in this field of science and technology.

There is an ongoing cooperation between Egypt and Germany concerning materials and materials technology. The workshop here in Cairo is a lively demonstration of this.

For Egypt new energy technologies may play an important role in the future looking, e. g. at solar energy, direct conversion systems like fuel cells or even combined systems of those. So it appears very logical and conclusive that material technologies for energy systems should play a major role in the scientific and technological development prospects of your country. The exchange of staff, the materials related R+D work should be continued and may be even intensified in the future.

Ladies and Gentlemen, I hope we will have an interesting and challenging meeting here in the next days. Last but not least let me mention the hospitality of our Egyptian partners which is well known to many of us. I thank you already in advance for everything that will be arranged.

Thank you and good luck.

Acknowledgements

The Joint Egyptian – German Workshop on „Materials and Processes for Advanced Technology: Materials for Energy Systems“ was held at the Atomic Energy Authority in Cairo, Egypt, 6.-9. April 2002.

The workshop was organized under the auspices of his Excellency Dr. Eng. Hassan Younis, the Minister of Electricity and Energy. He gave an opening statement delivered by Eng. H. El-kholy, first under secretary. Prof. Fayza Abdel Mageed, EAEA Chairperson also presented a statement. Strengthening cooperation between Egypt and Germany was emphasized by all speakers.

The workshop consisted of presentations from both sides. Nine German experts belonging to research centers, universities and industry have participated in the workshop. From the Egyptian side there were 18 lectures and about 50 senior management participants belonging to different electricity authorities and companies, Ministry of Petroleum, Ministry of Industry, Ministry of Defense, universities and research centres.

The presentations covered several R&D activities in the field of materials for energy technologies. Most of the presentations were focused on problems related to materials and manufacturing processes of different energy systems including solar cells, solid oxide fuel cells, steam power plants and gas turbines and superconducting materials. Some overviews were also presented on the strategy and programmes of renewable energy in Egypt as well as fuel cell programmes for transport applications in Egypt.

The workshop was considered as having been really successful in evaluating results on ongoing projects and giving hints for some future research and development work.

We thank all contributors and participants for their presentations and stimulating discussion. The funding given by the Federal Ministry for Education and Research (BMBF) through the International Bureau of Forschungszentrum Jülich GmbH is gratefully acknowledged.

The same holds for the Egyptian Ministry of Electricity and Energy and the Egyptian Atomic Energy Authority.

Moreover thanks belong to the International Bureau of Forschungszentrum Jülich GmbH for publishing these proceedings in their Series, International Cooperation, Bilateral Seminars.

1. General



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RENEWABLE ENERGY IN EGYPT
STRATEGY, ACHIEVEMENTS AND PROGRAMS
ENG. SHERIF ABOULNASR*
EXECUTIVE CHAIRMAN
NEW & RENEWABLE ENERGY AUTHORITY (NREA), EGYPT

1- Introduction

Securing energy demand on continuous bases is a vital element for sustained development plans. In view of the limited fossil fuel reserves, the depleted nature of the fossil fuel, the growing concerns about the pollution from the conventional power plants and their negative impacts on the environment, Egypt has given due consideration to the promotion of its indigenous renewable energy resources mainly Solar, Wind and Biomass.

2- Institutional Framework:

Egypt has an early start addressing renewable energy. Since 70's different institutions and organizations have developed programs in the field. Such programs were coordinated through the RE supreme council.

To support and enhance the institutional capabilities for renewable energy development and as a result of the growing interest and activities in the field, The New and Renewable Energy Authority "NREA" was established in 1986 to provide a focal point for expanding efforts to develop and introduce renewable energy technologies to Egypt on a commercial scale together with implementation of related energy conservation programs.

NREA is entrusted to plan and implement renewable energy programs in coordination with other concerned national and international institutions within the framework of its mandate which are:-

- Renewable energy resources assessment and planning for utilization.
- Research, development, demonstration, Testing and evaluation of the different technologies.
- Application of mature technologies.
- Education, training and information dissemination.
- Transfer of technology, development of local industry.
- Establishment of testing and certification facilities and development of local standards and codes.

3- The Strategy

In early 80's, while formulating the strategy of the Egyptian power sector, the planning for renewable energy was considered as an integral part of the National Energy Planning Process.

The renewable energy component of the national energy strategy targets to provide a contribution from R. E. sources to cover 3% of the electric energy demand by 2010, with additional contributions in other energy applications.

* Presented by Eng. Bothayna Ameen Rashed, General Manager of Planning, NREA

Such expansion plan gives plenty of room for a considerable share of electricity generation from renewable energy sources

It is obvious that the implementation of such strategy will be an essential element of the national plans for achieving sustainable development and protection of the environment via upgrading energy efficiency and replacing conventional polluting resources by renewable resources.

4- Renewable Energy Achievements:

During the last decade, Egypt has been one of the developing countries following programs for the development of renewable energy resources, with special emphasis on solar, wind and biomass. The following describes the milestone achievements in the different fields of activities, almost focusing on solar and wind energy resource assessment and applications with long term plans.

4-1 Pilot & Demonstration Projects

4.1.1 In the Field of Solar Photovoltaic.

Most of the Photovoltaic applications were demonstrated and field tested as Water pumping, desalination, clinical refrigerators, village electrification...etc, while telecommunication systems, navigation and airport aid lights and highway advertising boards are already commercialized. The capacity of the PV projects presently in operation amounts to about 2 MWp.

4.1.2 In the Field of Solar Thermal Applications And Energy Conservation Systems

- Domestic Solar Water Heaters (DSWH)

Since early 1980s, low temperature Domestic Solar Water Heaters (DSWH) have been produced locally through joint ventures. Currently, eight companies are active in the field of production, design and installation as well as competing to adopt products to the local conditions. The annual production capacity exceeds 25,000 m² of collectors. Over 300,000 m² have been installed and operated particularly in new cities and touristic villages. As well, the government has adopted measures to support market promotion through mandatory use of "DSWH" in new communities. Egyptian standard specifications and codes of practice for "DSWH" were issued in 1986. NREA is providing technical expertise and services for the design, testing, development, applications and supervision of solar water heating systems.

- Solar Industrial Processes Heat (SIPH)

To satisfy the strategic objectives, NREA implemented two "SIPH" pilot projects of low temperature in the food and textile industries. They are integrated with waste heat recovery systems and co-financed with United State Agency for International Development (USAID). Their objectives were to demonstrate and field testing Solar Industrial Process Heat and Waste Heat Recovery Systems in different sectors. Each

one included local manufactured flat plate collectors with total surface area 356 m² producing 26 m³/day of hot water at 50 – 65°C. The two projects have been operating successfully Since 1990, 1993 respectively, saving about 1800 TOE/Year.

In the frame of comprehensive planning of Solar Industrial Processes heat and waste heat recovery systems for medium temperature in Egypt (1997 -2012), NREA performed a study to forecast, through field Energy Audits, the potential of SIPH and waste heat recovery systems for six industrial sub sectors. The study was financed by the African Development Fund (ADF). As a result of this study, A Pharmaceutical company has been selected to host a pilot project for medium/ high temperature (up to 175°C).

The project is currently under implementation, using parabolic concentrators with single axis tracking system.

The project mainly consists of :

- Solar plant (parabolic trough collectors) for process steam generation at 175°C/8bar.
- Energy conservation for condensate steam returns system, insulation of steam network and burners of boilers.

The project is planned to start operation by 2003 with expected fuel saving rate of about 1200 TOE/Year.

4.1.3 In the Field Wind Energy

Egypt is endowed by huge wind energy potentials where the coastal areas particularly the Red Sea Coast and the South Western parts of the country have high wind velocities reaching 10 m/s and 7 m/s respectively. Wind resources in coastal areas of Egypt have proven to be feasible both for mechanical pumping and electricity generation. Several organizations have directed efforts towards utilization of such resource.

Encouraged by the high wind regime at the Red Sea, the first steps of exploiting wind energy have been started by limited pilot projects.

- In 1988, the First Wind Farm with a capacity of (400Kw) was installed in Ras Ghareb on the Red Sea Coast serving one of the oil companies. The Wind Farm Consists of 4 units, 100 kW each.
Fully imported wind turbines were used.
- In 1992, the second wind farm is 4X100 KW each at Hurghada on the Red Sea Coast. 45% of the wind turbine components were locally manufactured, mainly blades, towers and other mechanical parts. The farm has been connected to the local network of Hurghada city. In 1998, the network has been connected to the National grid.

The a/m wind generated electricity is powering desalination units to produce 130 m³/day of potable water to satisfy NREA' site facilities needs of water at Hurghada

4-2 Large Scale Electricity Production Program

Egypt has crossed the phase of limited demonstration projects to the phase of large scale grid connected projects.

In 1994, NREA has formulated its Bulk Renewable Energy Electricity Production Program (BREEPP) for large-scale power generation.

The BREEPP has two main components for both grid-connected large-scale solar and wind electricity generation plants and forecasted to push ahead both technologies to the market place.

4.2.1 Solar Thermal Electricity Generation (STEG)

As far as the solar electricity is concerned, NREA has completed in 1995, an assessment and identification study for the Solar Thermal Electricity Generation "STEG" potentials which concluded that:

1. The total accessible potential for national grid connected "STEG" systems in Egypt is tremendous and far exceeds all practical expectations for implementation. Priority is given to the areas having higher direct solar radiation intensity (2200–2600 Kwh/m²/year) and access to both electrical grids & natural gas networks.
2. The Integrated Solar Combined Cycle System "ISCCS" using parabolic trough solar technology with a conventional gas turbine combined cycle (Annex 4&5) is considered the most appropriate system for Egypt's first plant. The choice of solar technology for the next plants will depend upon the state of art at the time of commencing the implementation procedure.

In 1996, the Egyptian Cabinet of Ministers has approved on the establishment of the first "ISCCS" pilot power plant of about 100-150 MW capacity.

The natural gas will be used as a fossil fuel for the gas turbine and the peak period supplementary firing in the Waste Heat Recovery Boiler (WHRB).

The first plant is anticipated to be implemented through Build-Own-Operate-Transfer (BOOT) Or Build-Own-Operate (BOO) contract.

In 1997, two pre feasibility studies were performed for the first "ISCCS" plant at Kuraymat with a capacity of about (150) MW. The studies were based on parabolic trough concentrator and central tower receiver technologies as alternates. Egypt has officially requested The Global Environment Facility (GEF) to support the project.

GEF has shown a positive response being available to provide a grant fund to cover a substantial part of the incremental cost in comparison to the least cost conventional alternative producing the same annual electric energy, and assigning the World Bank as an implementing Agency

The consulting services were divided into two phases as follow:

Phase I:

To conduct a feasibility study covering the technical, economic, financial, aspects including identifying the appropriate configuration, plant size, solar fraction, suitable solar technology and conceptual design of the plant, with estimation of the incremental cost in comparison with a reference conventional (C.C) plant producing the same annual electric energy.

- The capacity of the power plant is 127MW.
- The solar contribution is 31 MWe
- The annual produced electric energy by the integrated plant is about 900 GWh.
- The solar contribution represented 9.1% of the total electric energy production
- Co₂ saving is 7.1%

Phase II:

The consulting services include:

- Preparation of the Request for Proposals (RFP) for private developers or any other documents as required.
- Assisting EEA/NREA in the evaluation of the offers, including support in negotiations with the successful bidder.

The second phase of consulting services is expected to be completed by end of 2001.

The plant is planned to be operative in 2006.

- Commercial wind Farms.

- A Grid connected 5 MW Wind Farm at Hurghada.

The farm consists of 38 wind turbines of different technologies (pitch regulated/stall regulated blades/ tubular/lattice towers) and ratings (of 100-300 Kw). 50% of the components are locally manufactured. The farm has been connected to the local grid and operated successfully since 1993, producing about 10 million Kwh/year.

- Wind Energy Technology Center (WETC)

A wind energy technology center in Hurghada was established in cooperation with Denmark. It includes a mechanical & electrical workshop and a training center.

The main activities of the center are:

- Research and development.
- Testing and certification for wind turbines' components
- Technical evaluation
- Training programs.

The center can serve local objectives and regional cooperation programs

An area of 80 Km² on the Gulf of Suez at Zafarana site has been allocated for NREA to start implementing the large-scale wind electricity programs.

Projects under operation:-

- The 1st phase (30 MW) of 60 Mw wind farm in cooperation with the Danish International Development Agency (DANIDA) has been connected to the national grid and operated since Nov. 2000. The annual electric energy production is about 120 GWh/year
- The 1st stage (33 Mw) of 73 Mw wind farm in cooperation with German government has been connected to the national grid and operated since Feb. 2001. The annual electric energy production is about 130 Gwh/year.

The above mentioned phases are saving about 50,000 T.O.E. /year

Projects under implementation

- The 2nd phase (30 MW) of 60 Mw wind farm in cooperation with (DANIDA) to be operative in 2003
- The second and third phases (each 20 MW) of the wind farm in cooperation with German government (to be operative by 2002 & 2003 respectively).

Projects under Negotiations

- 120 Mw wind farm at Zafarana (in 2 stages) in cooperation with Japan. The project is in the phase of negotiation, while a feasibility study was performed for the project.
- 60 Mw wind farm at Zafarana in cooperation with Spain. A memorandum of understanding was signed with the selected Spanish consulting firm was assigned to perform consulting services for the project.

5- Renewable Energy Program Up To 2010

5.1 In The Field of Solar Thermal Electricity Generation (STEG)

The ISCCS power plant (127MW) is considered as a first of series of hybrid solar fossil fuel power plants targeting to install about 750 MW capacity in an overlapped time frame based on BOOT system by the year 2010.

Table (1) Solar Thermal Electricity Generation Plan

5 Years Development Plans	Installed Capacity			Cumulative Capacity (Mw)	Annual Energy Generation at the end of the period Gwh/Year
	No. of Plants	Power Capacity (Mw)	Total Capacity (Mw)		
1997-2002	-	-	-	-	-
2002-2007	1	127	127	127	900
2007-2010	2	300	600	727	4600
After 2010	Dissemination according to cost reduction and the level of interest of private developers				

5.2 In The Field Wind Energy

The program targets to accumulated a total installed capacity of 600 MW wind parks, 300 Mw out of which will be undertaken by private sector based on BOOT system by the year 2010. The annual electric energy production will be increased to about 2.5 billion KWh, corresponding to fuel saving of 0.5 mio TOE/Y.

Table (2) Wind Farms Planned Installed Capacities and Electric Energy Generation

5 Years Development Plans	Installed Capacity (Mw)			Cumulative Capacity (Mw)	Energy Generation Annual energy at the end of the period Twh/Year
	Red Sea	East of Oweinat	Total Capacity		
1997-2002	120	----	120	120	0.48
2002-2007	330	----	330	450	1.8
2007-2010	100	50	150	600	2.4

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PV Activities in Egypt Status & Prospects

***Eng. Hassan Hassaballa Rakha
General Manager PV Dept. NREA***

1- Abstract

This paper presents the extensive experience of PV applications in Egypt, which are carried out, in parts by the New & Renewable Energy Authority (NREA) and the benefits of renewable energy. It also covers the future prospects of PV applications for sustainable development of rural and isolated areas, and the constraints limiting the spread use of such technology in Egypt.

2- Introduction

Egypt is located in the world's solar belt and has an excellent solar availability. The annual average global solar radiation over Egypt ranges from about 1950 kWh/m²/year on the Mediterranean coast to a more than 2600 kWh/m²/year in upper Egypt. While about 90 % of the Egyptian territory has an average global radiation greater than 2200 kWh/m²/year.

In 1986, the New and Renewable Energy Authority NREA was established in order to carry out the role of the introduction, dissemination, utilization and development of Renewable Energy RE application in Egypt. Energy was considered as an integral part of the national energy planning that targets to cover 3 % of the electric energy demand from renewable resources by the year 2010.

Egypt has got an ambitious plan for village electrification. More than 98 % of the village were electrified from the utility grid. From the rest of the unelectrified villages there are few hundreds of small remote rural communities that was found to best fit for photovoltaic PV solar electrification. Those villages are characterized by low power demand, constant load, dispersed nature of houses, beyond the economical extension of the utility and are not included in the future plan for electrification from the national grid.

Also PV pumping systems and PV solar home are needed for the private sector in the new reclaimed lands and remote areas, but the main difficulty now is the high initial costs of these systems.

3- Benefits of Renewable Energy

- Enhance diversity in energy supply markets, thereby strengthening energy security.
- Represent secure, long-term, environmentally sustainable energy supplies.
- Make a major contribution to the global and reduction of atmospheric emissions.
- Provide commercially attractive options to meet specific user.
- Create significant regional employment opportunities in energy infrastructure manufacturing, installation and maintenance.
- Offer low operating costs and opportunity to manufacture much of the equipment locally.
- Renewable energy can not be exhausted.

4- PREVIOUS EXPERIENCE I N THE FIELD OF PV SOLAR ENERGY FOR RURAL ELECTRIFICATION

Photovoltaic power utilization has been addressed within the Egyptian Ministry of Electricity and Energy MEE as early as 1979. Most of the known PV applications such as water pumping, desalination, clinical refrigerator, ice making plant, village electrification, bill boards etc have been demonstrated and field tested in Egypt. Some commercial PV applications such as telecommunication, navigation aids and billboards are now self-sustainable in Egypt.

Currently, the various PV powered projects are accounted to beyond 2 MWp spread over different parts of Egypt. Contributors in these projects are the national, international institutions and private sector .

5- NREA ACCOMPLISHMENT IN THE FILD OF PHOTOVOLTAIC PROJECTS

NREA has accomplished considerable achievements in introducing PV to the Egyptian Context for various applications starting from pilot projects to field - testing and demonstration through commercialization. The most significant projects are follows :

Water Pumping

- 14 kW_p PV pumping system at Wadi El-Natroun with water production in the range of 80 - 100 m³/day.
- 2.2 kW_p PV portable unit with water production in the range of 20 - 30 m³/day.

- 1.7 kW_p PV pumping unit at Mansoreia Village.

Desalination

- 7 kW_p PV pumping and RO water desalination plant for producing 5 - 7 m³/day of fresh water at High Voltage Research Center I EEA.
- 18.5 kW_p PV desalination RO plant at El-Hamrawein on the Red Sea with a productivity of 60 m³/day.
- 8 kW_p PV I Diesel - powered RO water desalination unit for producing 5 m³/day of potable water at Abou-Ghosoon on the Red Sea Coast.

Village Electrification

- 28 kW_p PV pilot project for electrification of remote village has been implemented for :
 - Household Lighting.
 - Street Lights.
 - Pumping Units.

Refrigeration

- Installation of a 38 kW PV/Diesel/Battery hybrid power system powered Ice-Making Plant to produce 6 tons per day of flake ice for fish preservation at remote desert lake in Wadi El-Raiyan, El-Fayoum.
- 10 PV-Power Refrigerators for vaccine storage were installed in rural health care facilities.
- 1.2 kW_p refrigerator for keeping medicine in health unit equipment at Mit Abou El-Kom Village.

Communication

- 8 PV powered emergency communication systems.

Signaling & Warning

- A naval warning system placed on Lake Nasser.

Others

- A number of PV - Powered colour television sets.
- A loudspeaker system at Mit Abou El-Kom Mosque.
- Lighting some offices for the organization for Energy Conservation and Planning OECP.

Consultancy Services

- Prepare tender document for PV powered obstruction lighting units with battery storage for High Voltage Transmission Lines (Towers) for Egyptian Electricity Authority EEA.
- Introducing the technical consultancy for acceptance and operation tests and preliminary hand over for Ein El-Skhona Tall Station and Suez Balance with 30 kW_p PV power system for lighting.

6- PV Prospects

PV Solar Electricity to serve rural / isolated areas

Energy has a vital role to play in meeting the basic needs of rural population and improving the standard of living. Increased and improved energy supplies can increase food production, water supply, Health care, Education and communication. It can also support industrial activity in rural areas, providing local employment, reduce migration to urban areas.

Egypt in its national strategy plan is aiming for the development of new communities, remote villages and desert areas.

6.1 Off-grid Remote Communities and Village PV Electrification

In spite of the ambitious on going Egyptian rural electrification plans through grid extension which covers more than 98 % of the rural villages, there will be still some remote isolated small communities and settlements that are far from the electric grid and consequently will not be attached to it.

More than a hundred of small remote isolated communities which are characterized by poor inhabitants were found to best fit the PV electrification and are not included in the future plan for electrification from the national grid. The structure of those communities in many cases includes 20 house each, 8 persons per family, low power demand (700-800 Wh/day), constant load, and dispersed nature of houses and far from the utility grid. Consequently individual PV household's kit capable of supplying around 700 Wh/day could be an appropriate solution.

The Egyptian government has decided lately to electrify a number of 33 remote villages as a first stage in Sinai using PV power systems. Five **remote communities have**

been chosen in south Sinai to be electrified by PV power as a 1st phase. Those five communities will be assessed in terms of the technical reliability and social impact and will feedback the next phases.

First Phase Project Profile

No of houses to be electrified	143
No of public buildings	4
Estimated load energy per house	800 Wh/day

6.2 PV Electricity Supply for Pumping System for Land Reclamation Projects

Currently the government of Egypt is placing high priority on developing New Desert areas in order to decrease the overpopulation around the Nile Valley and Delta creating new societies, new job opportunities, new investment as well as raising the standard of living.

The Egyptian plan of new land reclamation projects considered the use of ground water as a potential supply of irrigation. High level of solar radiation and availability of under ground water characterize the Egyptian desert areas. All those feature encourage the use of renewable energy, which is inexhaustible, clean energy and suitable for use rural areas which are far from the utility grid and difficult sites for the diesel operation.

In regard to the diesel gensets, the disadvantages of the diesel generator set are multiplied; costs of fuel and repairs time required for management of the supply of fuel, breakdowns and of start & stop, operation, a relatively short life time, fume, the disturbances resulting from fumes, noise and vibration.

The Egyptian national plans for new land reclamation include; development of 3.4 million feddans in Toshki, 12.000 feddans at Darb EL Arbean and planting 200.000 feddans in East Oweinat in 10 years time by digging 1500 – 1600 water wells. The estimated power requires for East Oweinat 200 MW for water pumping and water distribution network, small industries for agriculture product and lighting. The existing water wells are 217 and they use diesel generators.

The characteristics of the existing wells at East Oweinate are :

Static Head	: 25 – 30	m
Well Depth	: 250 – 300	m
Well Discharge	: 200 – 250	m ³ / hr.
Diesel Operation	: 16 hr/day	

7- PV Cost Reduction

- New material.
- Higher module efficiency.
- Improved manufacturing technology.
- Mass productions.
- Design quality.

8- PV Barriers

- Relatively higher unit cost of systems.
- Low income levels of rural dwellers.
- Lack of people awareness.
- Lack of coordination of the key players.
- Lack of incentive for market stimulation.
- Lack of local manufacturing capabilities to minimize system cost.
- Lack of setting of rural energy within national plans.

9- Recommendation / PV market development

To make PV a significant energy option for rural / isolated areas progress is needed to reduce costs, increase awareness faster market deployment by removing technical and non – technical barriers.

10- Action needed

The role of the governments:

- Incentives and subsidies (micro – finance schemes) should applied to stimulate demand.
- Given high priorities in the national plan for using PV solar home systems in the rural areas with small loans instead of extending the national grid.
- Holding seminar / workshops on rural energy to encourage the market.
- Encourage the private sector to participate in rural energy.
- Eliminate the taxes on the imported equipment.

10-1 Technical issues

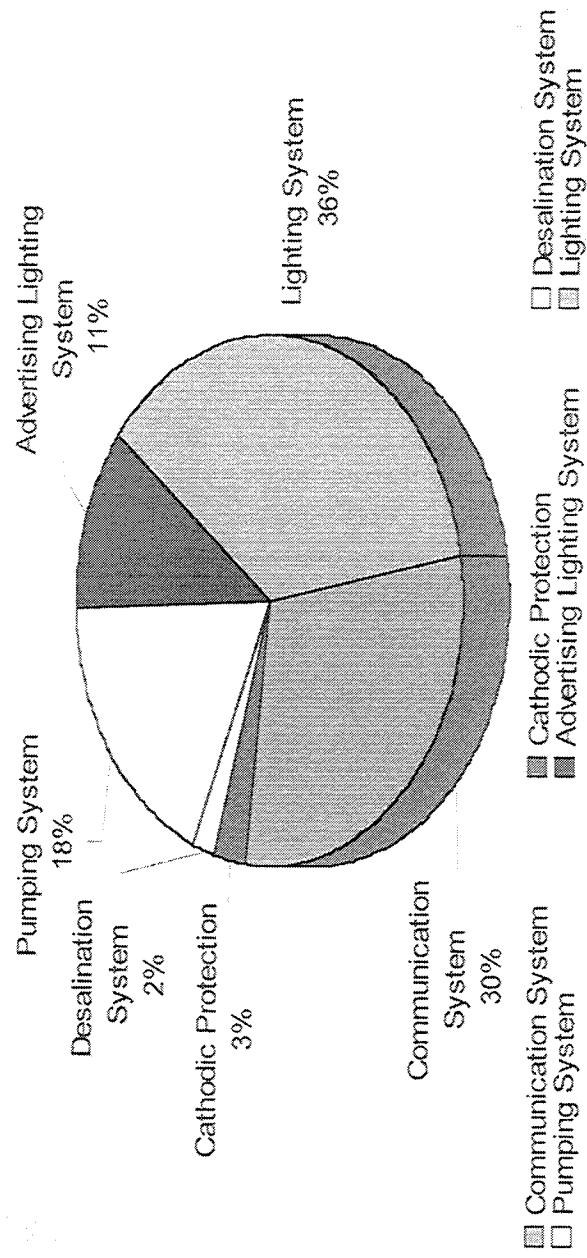
- Improving productivity and manufacturers of PV to make it more affordable.
- Train local people in technology application and operation.
- Link agriculture and cottage industries to rural energy development.

10-2 Financing agencies

- Adequate funding of GEF and ODA (official development assistance).
- Adequate funding of CDM (clean development mechanism) of Kyoto protocol to the UN framework convention on climate change.
- Leverage new World Bank Village Power Program.



Partitioning by PV Application in Egypt (2000 kW_p)



HYDROGEN, FUEL FOR EGYPT FUTURE ENERGY DEMAND

By

Dr. Emad El-Sharkawi
Chairman, ENC-WEC¹/Egypt

Dr. Ibrahim Abdel-Gelil
Executive Chairman, EEAA²/ Egypt

Eng. Maher Aziz Bedrous
Director of Environmental Studies,
EEHC³/Egypt

Eng. Ahmed Abd Rabbou
Coordinator, Climate Change Unit,
EEAA/Egypt

1. INTRODUCTION

New energy resources and technology will have a crucial role to play throughout tomorrow's world, but its potential contribution is even greater in the developing countries. It is in the developing countries that, over the next 30 years and beyond, the greatest increase in energy consumption is needed and will occur. Because of lack of resources, a significant proportion of this energy demand may have to be obtained from new forms of energy. Hydrogen is an acceptable candidate. It is practical to produce hydrogen in a large scale through electrolysis of water, which is an available substance in nature. Hydrogen combustion is very clean and almost complete under controlled conditions. It produces only water vapor and NO_x when combustion takes place with oxygen from air. NO_x removal technology exists today.

Hydrogen, also, has the outstanding physio-chemical properties such as: low ignition energy, high ignition temperature, high flame propagation rate and wide flammability range.

Already today hydrogen is a very important element used in huge quantities by the chemical industry. However, the major part (over 75%) of this hydrogen is produced by steam reforming of natural gas. The rest is produced by water electrolysis based on current (conventional) technology that does not necessarily rely on fossil energy.

Solar energy, (photovoltaics and photo-assisted electrolysis), may open a new gateway for large-scale solar hydrogen systems.

In short, hydrogen could provide an inexhaustible source for the energy needed to power tomorrow's world. Hydrogen also could help solve some of today's pollution-related environmental problems.

This paper outlines the present generation and use of hydrogen in Egypt's transport sector as well as future prospective to using large-scale hydrogen energy systems.

-
- 1. ENC-WEC = Egyptian National Committee of the World Energy Council
 - 2. EEAA = Egyptian Environmental Affairs Agency
 - 3. EEHC = Egyptian Electricity Holding Company

2. ENERGY SITUATION OF EGYPT

2.1. Energy supply

Egypt's main energy resources are oil, natural gas, coal and hydropower, in addition to a good potential of renewable energy resources. Oil reserves are estimated to equal to approximately 3.804 billion barrels (end of 2000/99), most of which are located in the Gulf of Suez. Oil production during the same year is accounted for about 36.585 Mtoe. Natural gas is the second major energy resource with a reserve level of nearly 8.89 billion barrels of oil equivalent. Most of the gas resources are located in the North Coast, Nile Delta and Western Desert. With the current annual production level of about 14.6 Mtoe, it is planned that natural gas would play an important role in the country's future fuel mix.

Hydropower is the third major energy resource in Egypt. Nearly 95% of the Nile's hydropower potential has already been exploited to generate about 14.659 TWh of electricity for the year 2000/99. Oil and gas accounts for about 94.4% of total commercial energy production while hydropower represents the remaining 5.6%. In addition to oil, natural gas and hydropower, Egypt has limited coal reserves estimated at about 27 Mt. The only commercial mining is now being developed in "Maghara", Sinai to produce about 60,000 tons per year. About 1.4 Mt tons per year of coal are being imported as feedstock for steel industry.

In addition to its limited commercial energy resources, Egypt has also a good potential of renewable energy resources. These include solar, wind and biomass such as fuel wood, agriculture wastes and dried animal dung, which have been used in rural areas to meet some energy demand. It is estimated that about 3.6 Mt of oil equivalent of biomass energy is consumed annually.

Due to its geographic locations, Egypt enjoys the sunshine all year around with direct daily solar intensity ranging between 2600 to 7100 kcal/m². Meanwhile, wind speed mappings showed that Egypt has some locations of average annual wind speed of about 30 km/hr capable of producing power from wind turbines.

According to 2000/99 figures, primary commercial energy consumption totalled about 44.05 Mtoe of which oil represents about 61%, gas about 31% and hydropower about 8%. The per capita energy consumption is approximately 0.67 toe which is higher than the average of most developing countries.

2.2. Energy Demand

Egypt has had a long history of rapidly growing energy demand which grew by an average growth rate of about 8.6% per annum during the 1970's and 6.5% during the 1980's. During the same periods, the electricity sector was characterized by increasing reliance on oil as a basic source of fuels due to limited availability of hydropower resources. Thermal power generation using petroleum products and natural gas currently represents nearly 80% of the total electricity generation, while the balance is met by hydropower.

In addition to energy transformation sectors, energy is consumed in four major end use sectors. These are industry, transport, residential and commercial and agriculture. Energy consumption by sectors in 2000/99 reveals that industry and transport are the major energy consuming sectors which accounted for about 45% and 31.3% respectively of total final consumption.

2.3. Energy future outlook

Based on the Government's development plans, population growth, fuel prices, and using the income and price elasticities previously developed at OEP, the total and sectoral future energy demand during the period (1998/99-2016/17) have been determined using the Energy and Power Evaluation Program (ENPEP). Accordingly, total energy consumption is expected to increase from nearly 1213 PJ in 1998/99 to about 4177 PJ in the year 2016/17. The industry sector is expected to be the major consumer of petroleum energy (oil and gas) in the year 2016/17. Its share in the total demand is expected to increase to about 45 % in the year 2016/17. The demand of the power sector is found to increase from 403 PJ in 1998/99 to about 1335 PJ in 2016/17. The future expansion plan of the Egyptian Electricity Holding Company (EEHC) through the year 2017 is expected to be 77% dependent on natural gas, 8% hydropower, and 5% on renewable resources. The transport sector total demand is expected to increase from nearly 310 PJ in 1998/99 with a share of about 37% of total energy consumption to reach about 501 PJ in 2016/17 with a share of 12% of total energy consumption.

Considering this big demand of energy on the light of oil and gas reserves in Egypt, it is quite obvious that new sources of energy are greatly needed for securing energy supply streams to the national sustainable energy development. In this context, hydrogen fuel represents the most viable solution for meeting future needs of energy demand.

3. VIABILITY OF HYDROGEN FUEL

The unique advantage of hydrogen as a fuel is that it is one of the most abundant elements in the universe, can be produced from water, and does not introduce oxides of carbon into the atmosphere. A hydrogen-based economy would evolve on a completely sustainable, nonpolluting fuel cycle, one that replicates the great natural cycle of the biosphere with water vapor as its only major waste product.

The conversion technology of water or natural gas to hydrogen in large central plants is technically viable today; economics and safety are the major concerns that must be overcome to make widespread commercial use of hydrogen as fuel.

Existing natural-gas pipelines could be adapted in many cases for hydrogen transportation, so that transporting hydrogen would cost much less than transporting electricity over long distances. Hydrogen can also be stored more readily than electricity. With proper modifications, some types of internal-combustion engines can be modified to burn hydrogen. Hydrogen also can have advantage as an aviation fuel for jet engines, in the future.

Gaseous hydrogen, taking its efficiency advantage into account, would cost about \$1.40 for the equivalent of one gallon of gasoline. If fossil fuels are held responsible for the environmental damage they do, then at least \$1 per gallon to the true cost of gasoline has to be added. Therefore, even today, hydrogen is cheaper than fossil fuels when the overall societal costs are internalised.

4. SOURCES OF HYDROGEN

The vast majority of the hydrogen needed to power tomorrow's world would be manufactured as a by-product of renewable or environmentally acceptable technologies. Hydrogen will be

manufactured from non-polluting sources and would provide a means to wean us from traditional fuels.

Until renewable technologies are proven reliable and economical, most of the hydrogen manufactured will continue to be a by-product of fossil fuels such as natural gas. In the first part of the twenty-first century, coal could become the cheapest source for producing hydrogen, with its carbon dioxide by-product captured and utilized for industrial purposes or sequestered. And, as the next generations of inherently safe nuclear reactors are developed, and a safe acceptable answer is found for the question of permanent storing radioactive wastes, then nuclear power could also prove to be an important source of electricity for hydrogen production.

Today, many of the R&D centres are researching hydrogen production from coal, natural gas, and the use of electro-catalysts to “split” water with sunlight. Scientists and technologists believe that, initially, the way to a hydrogen-powered world is by extracting hydrogen from coal but containing the attendant carbon dioxide. They believe that the overall project will include selling or sequestering carbon dioxide so that it will not contribute to the global-warming problem.

They, also, consider that photovoltaic (PV) based electrolytic hydrogen – hydrogen captured from the earth’s atmosphere – could be both environmentally benign and an economically competitive alternative to electricity by the turn of the century. These scientists also claim that PV hydrogen production would require a relatively small land mass. A circular area with a diameter of 240 miles, located in New Mexico or Arizona, would theoretically be sufficient to hold enough PV cells to manufacture hydrogen equivalent in energy to the entire fossil-fuel-derived energy of oil, natural gas, and coal consumed in the United States during 1986.

Some leading manufacturers of silicon solar cells, predicted that photovoltaics will be used in the electrolysis of water to produce hydrogen for fuel cells and combustion engines, opening up to photovoltaics, not just the market for electric power, but also the transport market.

Further research, testing, and development will determine which energy source will produce hydrogen most economically while accounting and paying for polluting by-products. But this doesn’t mean that only one source will win and exclusively dominate future energy supplies. If all energy sources make improvements, this planet will have a more sustainable energy mix.

5. EGYPT AND HYDROGEN FUEL

Egypt is endowed with two principal resources from which hydrogen fuel can be produced. Egypt has natural gas, and is blessed with cloudless skies and intense solar radiation in southern Egypt.

5.1 Hydrogen Production

Egyptian experience with hydrogen production is wide. Reformers are currently in use in fertilizer and petrochemical facilities to produce hydrogen. Electrolysis systems are also being used in Egypt. A number of indicative examples are presented below.

Abu Qir Fertilizer Factory. The Abu Qir fertilizer in Alexandria uses 1000 tons of methane from natural gas to produce 1750 tons of urea per day. Pipeline of natural gas is upgraded to 95% methane using molecular sieves. Methane with no sulfur is used as feed stock. Steam reforming of methane at 900°C in the presence of a nickel oxide catalyst, converts methane into hydrogen, CO, CO₂. A low temperature converter with copper and zinc oxide as catalysts converts methane into hydrogen, CO, CO₂. A low temperature with copper and zinc

oxide as catalysts converts CO to CO₂. Potassium hydroxide solution separates the CO₂ from hydrogen. Hydrogen is used to produce ammonia, and the ammonia and carbon dioxide combine to form urea.

Oil Refineries. The refineries are in Suez, Ameriya, Alexandria, Assuit and Cairo. All fossil fuel based refineries produce hydrogen as a byproduct. The naphtha refinery uses a catalyst to raise the octane number of gasoline from 40 to 90; and in the process, hydrogen is produced as a byproduct. The refineries that produce the higher distillates (premium gasoline, regular gasoline and diesel oil) from fuel oil use the hydrogen byproduct to remove sulfur from fuel oil.

Kima Fertilizer Factory (hydroelectric electrolysis). This facility has been in successful operation for over 25 years producing hydrogen through hydropower electrolysis of water. Now natural gas mains are being laid from the gas fields, in the north of the Nile Delta, up to Assiut, and Kima is planning to use natural gas as the feed stock for hydrogen production. Kima factory produces, presently, 3000 tons of hydrogen per day using uni-polar skid mounted electrolyzers manufactured by Brown Boveri Company. These are old electrolyzers but very reliable. The newer versions available from several other sources are more efficient. A 25% Potassium Hydroxide solution at 80°C is the electrolyte used for the electrolysis process. The electrolyte is supplied with de-mineralized artesian well water to replenish the system. No compressors are used because the hydrogen produced is directly consumed in the production of ammonia fertilizer. There is no storage of hydrogen either. Approximately 100,000 Tons of oxygen is vented into the atmosphere each day. The Kima factory has a capacity to produce 80 million m³ of hydrogen per day.

Kima is also, however, studying the feasibility of producing hydrogen by solar electrolysis, with Japanese technical assistance, the study also includes the possibility of exporting heavy water to Japan.

5.2 Fuel Cell Technology in the Egyptian Context

A large number of Egyptian institutions have undertaken research on fuel cell technology. Cairo University and National Research Center are the most active of these institutions having worked on testing catalysts for increasing the production of hydrogen ions, developing more efficient Proton Exchange Membranes and a Direct Methanol Fuel Cell (DMFC) operating at low temperature and using liquid fuel to produce hydrogen. Other research institutions have also undertaken work in this field.

The following is representative of the applied work undertaken at the National Research Center:

- Preparation of practical electrodes for the fuel cell which reduces the current noble metal content for cost reduction;
- Optimization of electrode morphology to improve mass transport in the diffusion layer to enhance catalytic reactions;
- Investigation of electrode porosity and permeability to methanol.
- Transition metal Pthalocyanides and Prophetic for use as oxygen reduction catalysts in the DMFC;
- Development of new inorganic membranes for DMFC based on zeolites and Tin Mordenites. The investigation of the solid electrolyte conductivity and methanol permeability in a single cell configuration.

Egypt is, therefore, very well positioned to be able to absorb fuel cell technology, and consequently to use hydrogen fuel on a large scale as the most favorable fuel for fuel cell operation.

6. EGYPT FUEL CELL BUS DEMONSTRATION PROJECT

Egypt fuel cell demonstration project is co-funded by the Global Environment facility, GEF, Government of Egypt, GOE and bus manufacturer. The GEF objective of funding this project is to support the commercialization of fuel cell technology and reducing the cost of technologies that reduces the emissions of Greenhouse gases, GHG. The main goal of this project from the Egyptian prospective is technology transfer of an advanced efficient technology that uses available energy resources in Egypt and demonstration of utilizing hydrogen as clean alternative fuel in transport sector.

6.1 Project objectives:

The specific objectives of the project are;

- Verify the efficiency, operability, reliability, and maintenance requirements of fuel cell buses.
- Build up the local experience and capability in both personnel and parts supply for operating and maintaining fuel cell buses and hydrogen facilities.
- Demonstrate to the public and gain acceptance from them the operability, safety, high performance, and low emission of fuel cell buses and hydrogen production and fueling facilities.
- Provide opportunities for the local bus manufactures to integrate and assemble fuel cell buses with imported engines and chassis.
- Induce the universities and research institutes in Egypt to get more involved in fuel cell technology.
- Establish policy changes and codes/standards to promote the use of fuel cell technology.
- Increase the volume demand of fuel cell buses, jointly with other GEF fuel cell bus demonstration projects, to accelerate the commercialisation.
- Accumulate experience as input to fuel cell bus developers to further improve their products and accelerate commercialisation.

Most of the objectives above are geared for the fuel cell bus technology to take root in Egypt so that a full commercial implementation of the technology can be materialized later to contribute to the global efforts for GHG reduction. These objectives are also set to lead Egypt to become a regional or worldwide fuel cell bus supplier. This will be accomplished by building upon the manufacturing expertise gained during the demonstration project and the low labor cost in Egypt. The new business created can contribute significantly to the nation's economy.

6.2 Project feasibility study

A detailed feasibility study was conducted with a major objective to select the best fuel cell bus system for public transportation in Cairo. This feasibility study was conducted on two different parts. The first part concentrate on a full-scale commercial deployment of fuel cell buses in

Cairo, i.e. the total bus fleet of Cairo Transport Authority, CTA, about 3600 buses will use hydrogen and fuel cell technology within the coming 15-20 years.

Where, the second part of the feasibility study concentrated on the demonstration scale of 8 buses to start real operation mid 2002.

The feasibility study designed to address the following issues for both the commercialisation and demonstration parts;

- Should the hydrogen required be produced in a large centralised plant or by a small plants located at each garage?
- What is the best way to produce hydrogen, by electrolysis, natural gas reforming, natural gas partial oxidation, or purchase from the a petrochemical or fertilizer plant?
- What is the best way to transport hydrogen from the central plant to bus garages, by liquid tank or by pipeline?
- Does it make sense to use more costly electricity from renewable energy resources for the electrolyser as to maximize CO₂ reduction?
- Can the additional cost to sequester CO₂ generated from hydrogen plant be justified by the increased amount of CO₂ reduction?
- Should the hydrogen required for the fuel cell buses be produced on-board or off board?

In addition to addressing the previous technical issues, a cost estimates were conducted based on the expected projected costs of the system component when they are fully commercialised.

The final selection of the optimum system was judged not just by the incremental cost of CO₂ reduction but many other factors, such as the total capital required, amount of CO₂ reduction and cost per kilometre of bus driving were also considered.

Nine scenarios were assessed and compared to the baseline scenario, current diesel bus, within the feasibility study. These scenarios were;

The 1st scenario is the baseline current diesel bus

The 2nd to 4th scenarios the hydrogen is produced in centralized plant located at Dahshour based on natural gas reforming, In second scenario hydrogen is converted cryogenically into liquid which is delivered in tank trucks to the bus garages of CTA. In third scenario hydrogen is supplied the CTA garages by pipeline. Fourth scenario the same as the third scenario with CO₂ sequestration into spent gas well in Beni Suef area.

The 5th to the 8th scenarios are designed to test the on-site hydrogen production to eliminate the cost of hydrogen transport. 5th and 6th scenarios using uses natural gas as feedstock of compact reformer and partial oxidation technology. The 7th and 8th scenarios are designed to test the on-site hydrogen production using the compact alkali electrolyzer and proton exchange membrane, PEM. The 7th and 8th scenarios using wind power as source of electricity for the electrolyzers to test a zero GHG emission scenarios

The 9th is to assess the option of purchasing the hydrogen from the KIMA plant in Aswan. The hydrogen will be liquefied and shipped by barges through the Nile to Cairo and then distributed to the CTA garages by trucks.

The final results of the feasibility study for a full-scale commercial deployment of fuel cell buses in Cairo a centralized natural gas reforming plant with the product hydrogen delivered to the bus garages by a gas pipeline and CO₂ recovered and sequestered in a spent gas well was selected base on the abovementioned criteria.

Whereas, for the demonstration project, it is not practical to construct a centralized natural gas reforming plant due to the small needed hydrogen quantity for operating only 8 buses. Thus, a packaged electrolyzer unit, including high pressure hydrogen gas storage cylinders, hydrogen compressors, and dispensers, will be purchased and installed at the host garage to meet the hydrogen requirement.

6.3. Demonstration Project Activities

The demonstration project will not be limited to the demonstration of the fuel cell technology and hydrogen production handling in public transport sector with all the detailed activities mentioned hereafter but also will implement few of sustainability measures, task 5, that will support the future commercialisation of hydrogen and fuel cell technology in Egypt. The demonstration project will be carried out with five major tasks. These activities include the following:

Task 1: Fuel Cell Bus Purchase

- Tasks 1.1: Finalize Bus Specification
- Tasks 1.2: Issue Tender and Award Contract for the Fuel-Cell Buses
- Tasks 1.3: Fabrication and Delivery of the First 3 Buses
- Tasks 1.4: Fabrication and Delivery of the Next 5 Buses

Task 2: Hydrogen Facility Purchase and Installation

- Tasks 2.1: Engineering and Site Design
- Tasks 2.2: Permitting
- Tasks 2.3: Major Equipment/Facility Purchase
- Tasks 2.4: Utility Hookup and Site Construction
- Tasks 2.5: Mechanical Shakedown and Facility Startup

Task 3: Bus/H₂ Facility Operation and Maintenance

- Tasks 3.1: Operation and Maintenance of the First 3 Buses
- Tasks 3.2: Operation and Maintenance of the Next 5 Buses
- Tasks 3.3: Operation and Maintenance of Hydrogen Facility

Task 4: Test Data Analysis and Project Management

- Tasks 4.1: Prepare Test Plan
- Tasks 4.2: Data Acquisition and Analysis
- Tasks 4.3: Project Management and Reporting

Task 5: Sustainability Program

Tasks 5.1: Develop Master Plan/Intervention Measures
Tasks 5.2: Build Up Codes/Standards and Local Capability
Tasks 5.3: Disseminate Information

6. 5. Project Sustainability

To sustain the fuel cell technology in Egypt after the GEF support, the first activity is for GCBC to expand the demonstration project. As an example, 20 more fuel cell buses could be purchased at the end of the demonstration project to increase the fleet size from 8 to 28 buses. As the hydrogen facility is already oversized, purchasing another electrolyzer module to double the hydrogen production capacity should be sufficient to meet the need of the expanded fleet.

The cost of the 8 fuel cell buses to be purchased for the GEF project is 10 times of that of diesel buses. By the time the additional 20 buses are purchased (2006), the fuel cell bus cost is expected to drop to be 2-3 times of the diesel bus cost. As the cost difference is still too large for the project to proceed on commercial basis, the Egyptian Government will seek finance from various sources to fund the incremental cost. The incremental cost is estimated to be US\$ 15 million, including the additional hydrogen production facility, utility consumption, and labor and management cost.

This expanded project will operate for 2-3 years. By 2008 or 2009 when it is completed, the fuel cell bus cost is expected to be only 10-30% more than the diesel bus cost. At that time, the tax credit or soft loan provided by the government should give enough incentive for the local bus manufactures to launch commercial production and allows GCBC and CTA to convert diesel buses or CNG buses on a garage-by-garage basis (on the average 150 buses per garage) without government's financial aid. The incentive for the bus manufactures could also be provided by the increase of diesel fuel cost, tighter air emission standard, or tax on air emission or carbon emission.

Meanwhile, the Ministry of Petroleum or private entrepreneurs would be willing to commit to building the centralized hydrogen production plant and distribution system when the fuel cell technology becomes fully proven in the expanded demonstration project and the commercialization prospect becomes certain. To minimize the capital requirement, the centralized hydrogen plant will be built by modular construction in stages to be in progression with the bus garage conversion. This is also true to some degree for the hydrogen distribution by pipelines. Only the trunk line will be built first. The branch lines to the individual garages will be added as more and more garages are converted.

The construction of the hydrogen distribution system and also the pipeline for CO₂ sequestration falls into the category of infrastructure buildup. The government needs to either directly finance the project or provide guarantee on the return for investors to take on the project.

6. 6. Project Research Program

Within the project appraisal committee, PAC, meeting organized on Feb. 2002, where the project were presented and approved by the committee due to its outstanding contributions to both energy and transport sectors in Egypt. The research program of the project attracts the attention of most of the committee members and a lot of recommendation and modification were provided to the program.

The original research program concentrated on the Proton Exchange Membrane, PEM, fuel cell type that will be used for Cairo fuel cell bus demonstration project. The current research program covers the following issues for PEM fuel cell and the fuel cell buses: (a) improvements of fuel cell stack components; (b) new or improved power train system design to make the system simpler, more efficient, lower cost, dynamically more responsive, or operable over a wider range; (c) improvements of power train components and, (d) new or improved hydrogen production processes which are more efficient, require lower cost, or have lower CO₂ emissions.

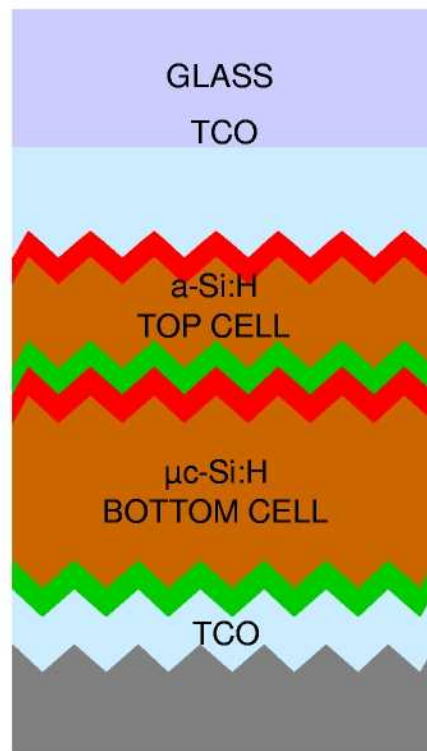
The PAC meeting recommended that the research program should covers all the types of fuel cells using other fuels rather than the hydrogen used for different technical applications. Based on that recommendation the research program will be open for both stationary as well as mobile application for the most common fuel cell types like, Alkaline Fuel Cell, AFC, Phosphoric Acid Fuel Cell, PAFC, Molten Carbonate Fuel Cell, MCFC, and Solid Oxide Fuel Cell, SOFC, as well as the PEM. Aiming at improving the overall performance, reducing costs and prolongs the lifetime of the fuel cells, the following topics could be areas for the new research program, in addition to the original program, for all the mentioned fuel cell types; the electrolyte, the catalyst and the bipolar plate.

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2. Photovoltaics



F. Abulfotuh	Photovoltaic Technology – Status, Advances, Utilization	37
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Photovoltaic Technology

Status, Advances, Utilization



**Middle-East Center for Energy and Environment
Technologies (MCEET)**

E-mail: fuadpv1@mk.net

OUTLINE

ENERGY SITUATION

(Environment Issues)

PHOTOVOLTAIC TECHNOLOGIES

(Renewable Energy Revolution)

- **ADVANCES**
- **MANUFACTURING**
- **MARKET**
- **APPLICATION**

Energy Knowledge / Issues

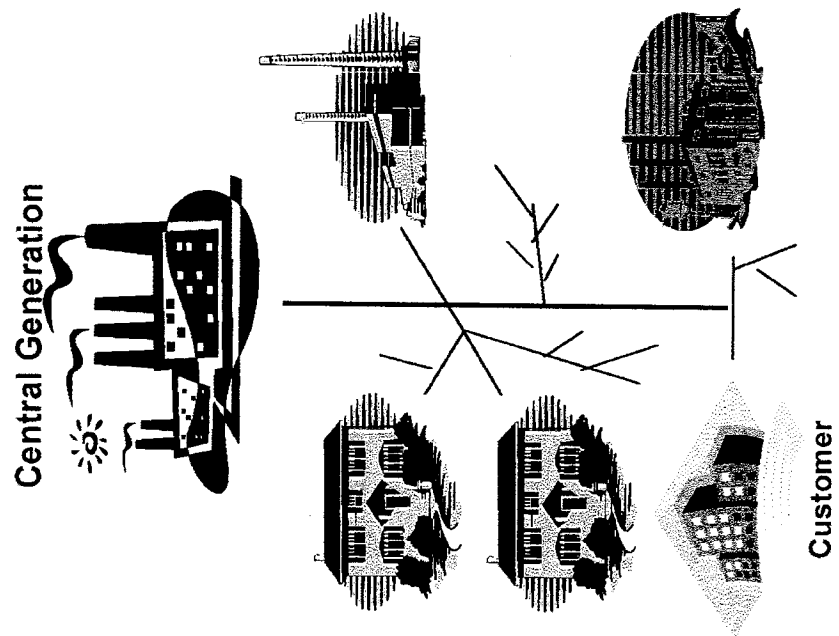
Issues

- Rising energy demand-inevitable
- Unmet demand will limit development, trapping billions in poverty and dependency
- Conflict between energy supply/use and damage to the world

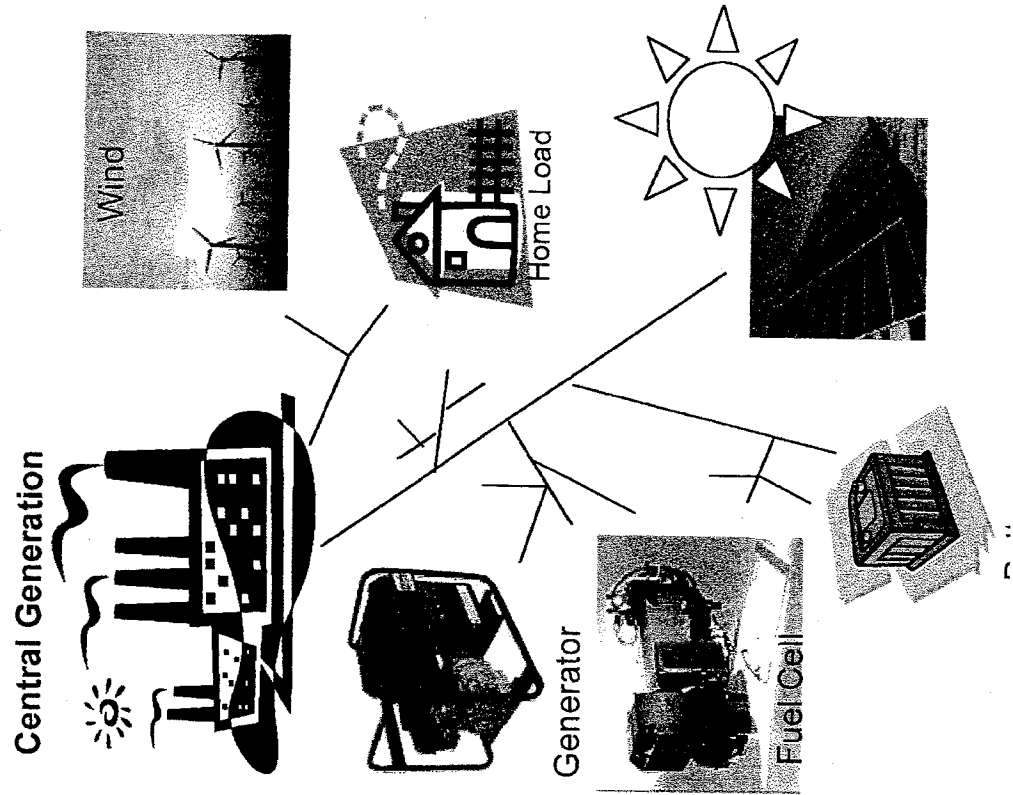
ACTIONS

- Knowledge & research
- In-country programs and specialist advisory divisions
- Enable sustainable livelihoods
- Look for better services
- Protect the environment

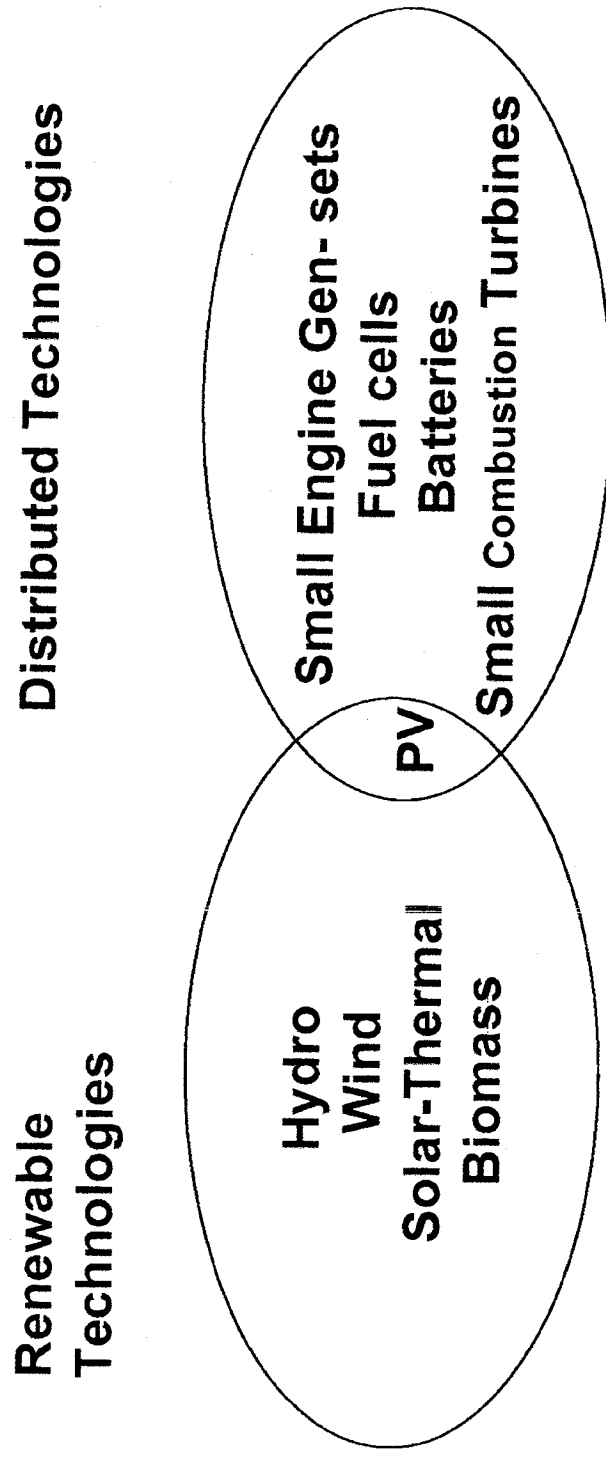
Today's Central Utility



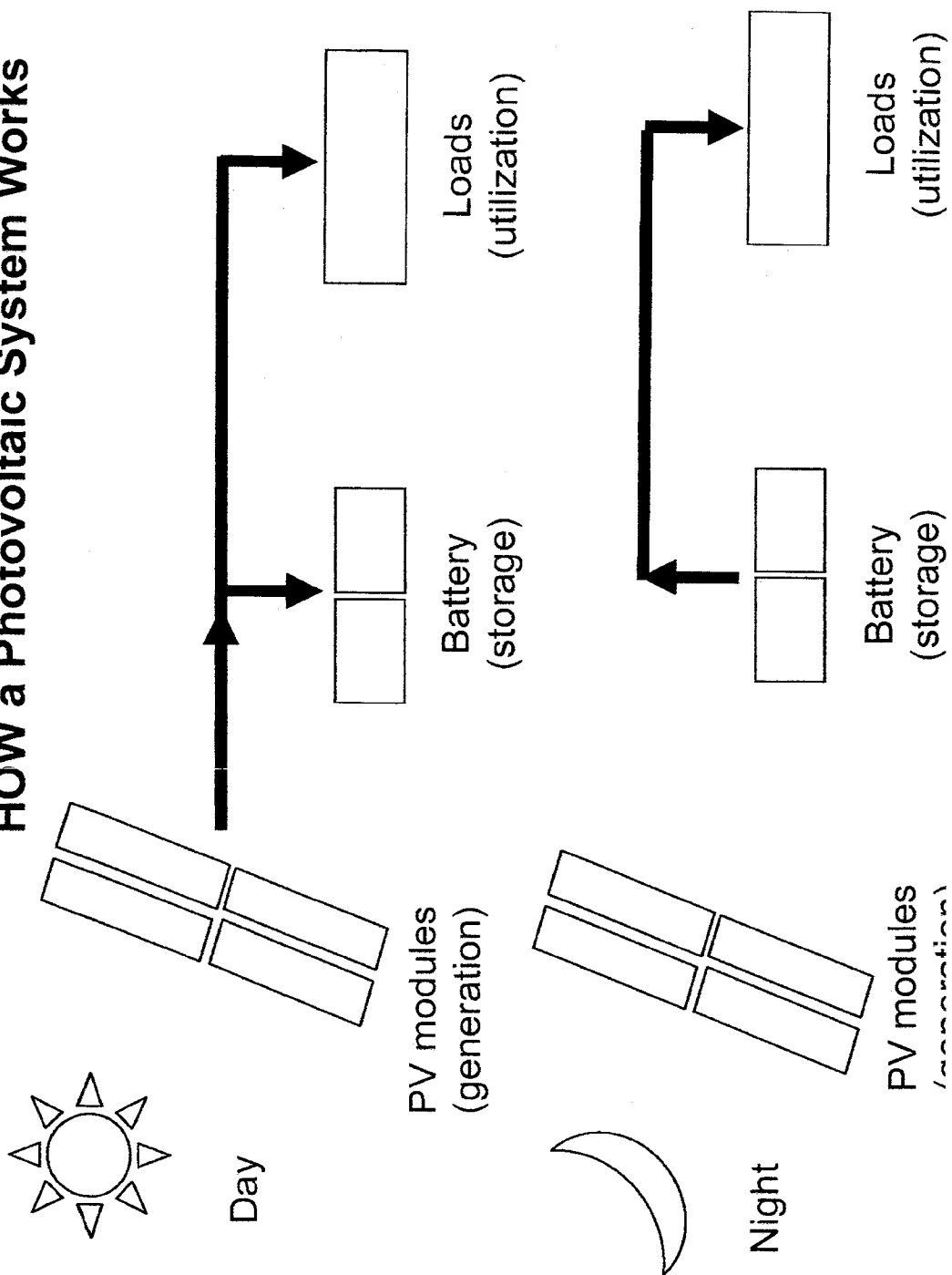
Tomorrow's Distributed Utility



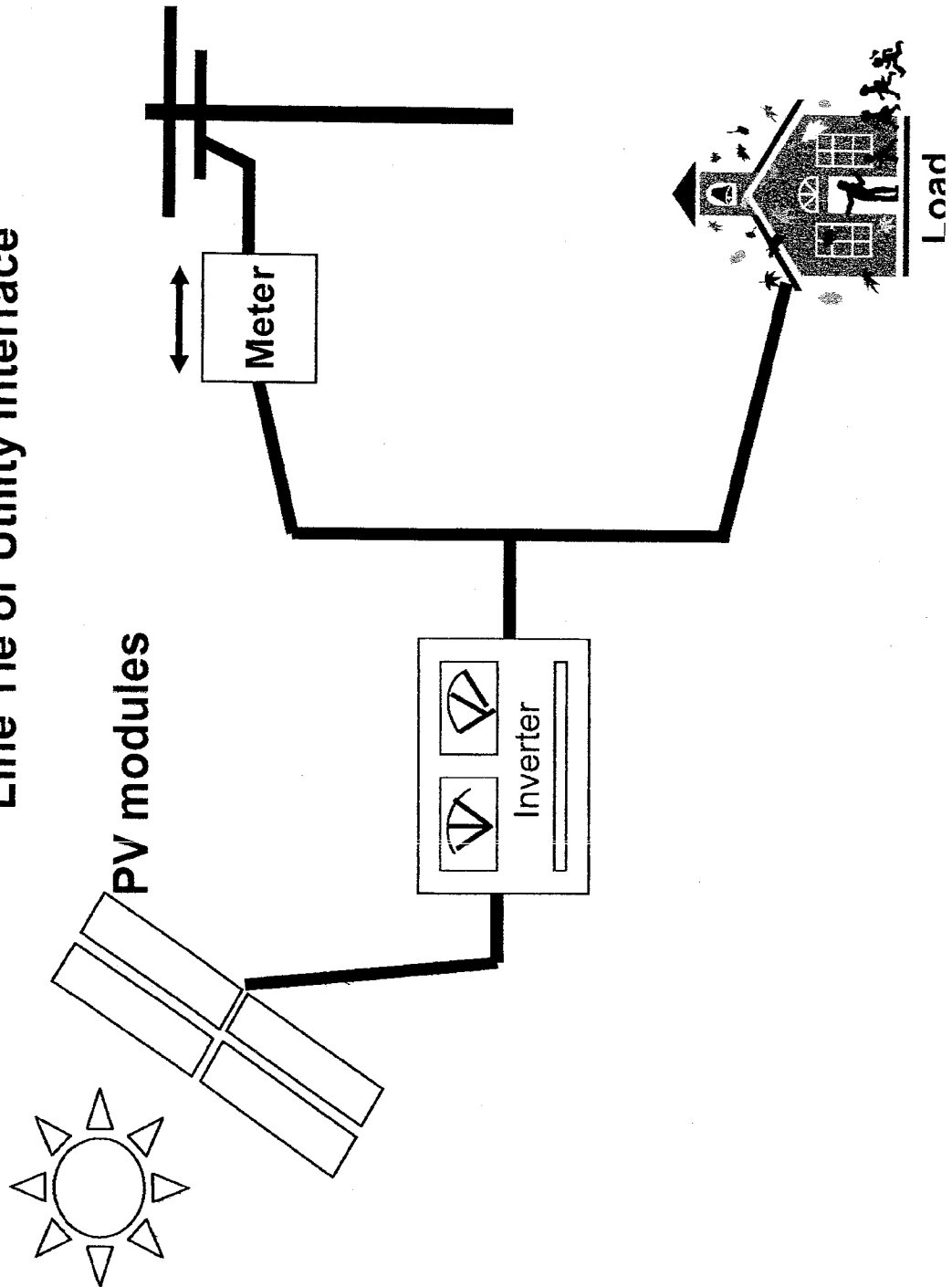
Advanced Power Generation Technologies Strategic Overview



HOW a Photovoltaic System Works



Line Tie or Utility Interface



Key PV Market Segments With Examples

Sector I. The products contains storage

- Battery chargers
- Consumers Products
- Boats, motor homes, cars
- Communications
- Signals

Sector III. Displacements of an alternative fuel

- Fuel is the storage
- PV/diesel hybrid

Sector II. The products is the storage

- Water pumping
- Desalination
- Refrigeration
- Daytime loads
- Cathodic protection

Sector IV. Utility connected applications (central or distributed)

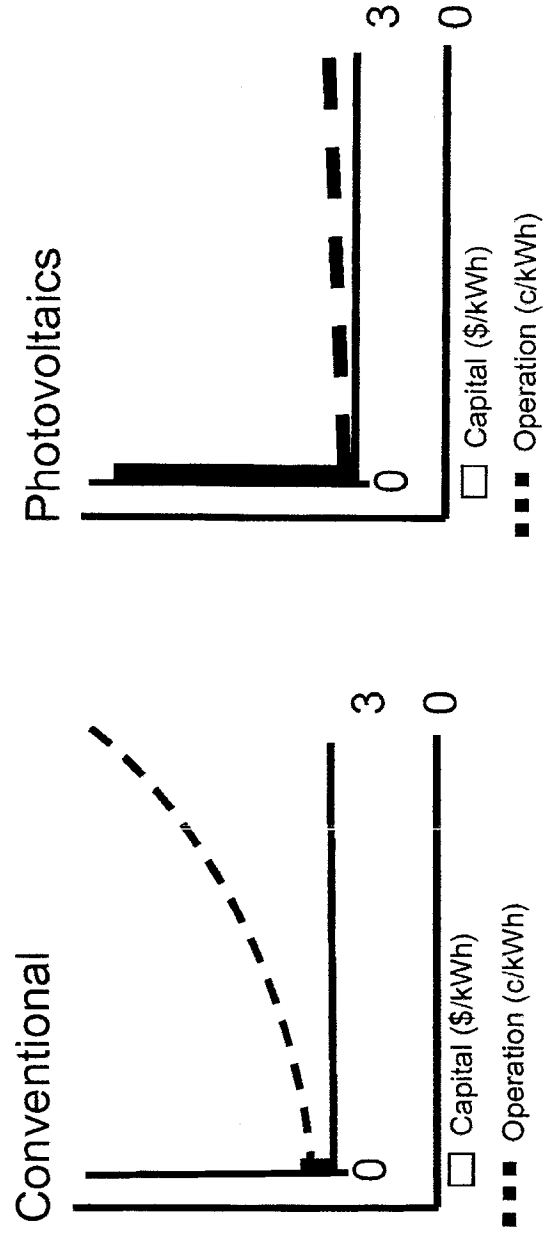
Storage is in the other fuels displaced in the system or in others generators

- Grid-connected residences
- Utility and third party-financed projects
- Commercial co generators

Barriers to the widespread use of Photovoltaics in the developing world

Barriers	Solutions
• Lack of funds of many potential users	International support
• Lack of appropriate financing schemes	Innovative finance schemes / credit
• Price distortions	Reduce subsidies on fossil fuels
• Lack of awareness-decision makers	Information programs
• Lack of awareness-users	Information/advertising program
• Lack of technical skills	National/regional training program
• Lack of infrastructure support (e.g., preventative maintenance, repair service)	Programs of critical mass that allow for the cost of infrastructure support

Known vs. Uncertain Costs



**PV's Fuel Independence and Front-End Cost Ensure
Against**

Unforeseen Cost Increases or Supply Disruption.

Comparison of PV Cost (kWh) With Fossil Fuels Cost (kWh)

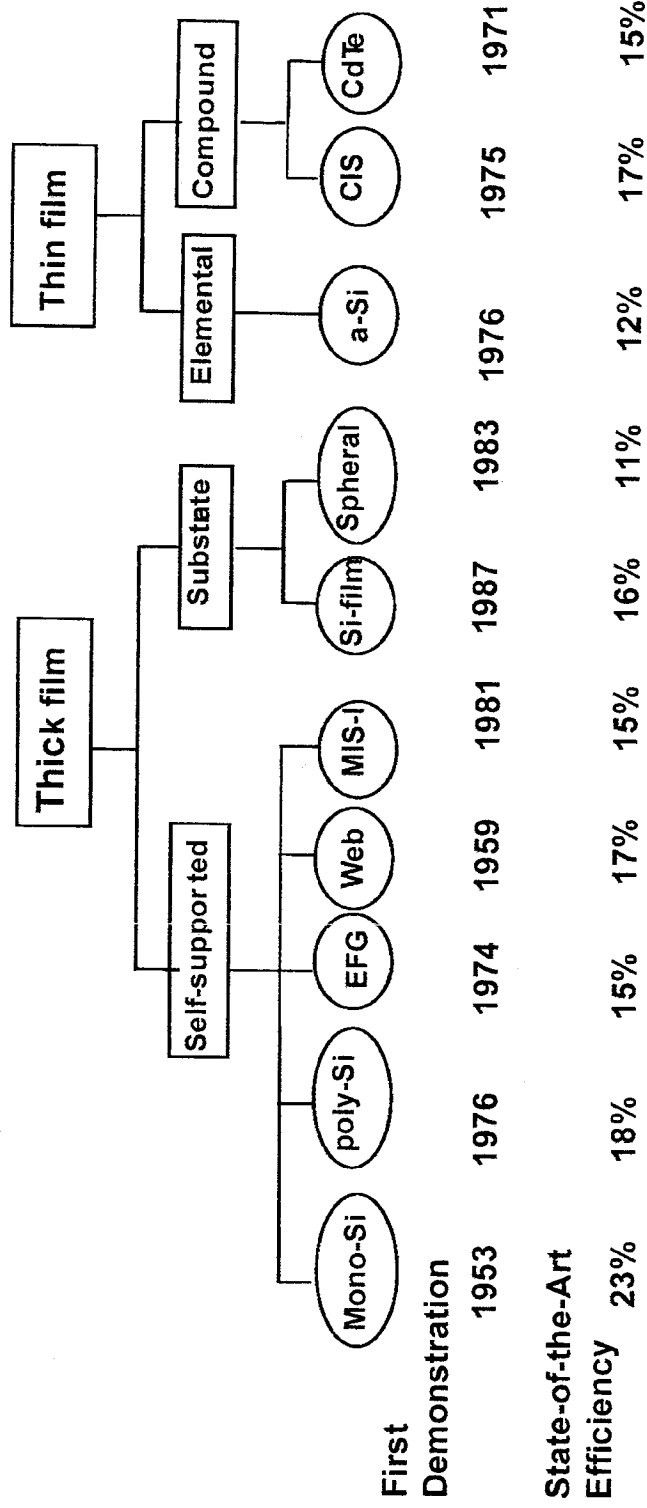
Bulk plants	\$/kWh
Industrial cost	0.05
“Negative cost” for emissions	0.05
“Negative cost” for CO ₂ (greenhouse emissions)	0.05
Total Cost	0.15

Grid support plants	\$/kWh
Industrial cost	0.25
“Negative cost” for emissions	0.10
Total Cost	0.35

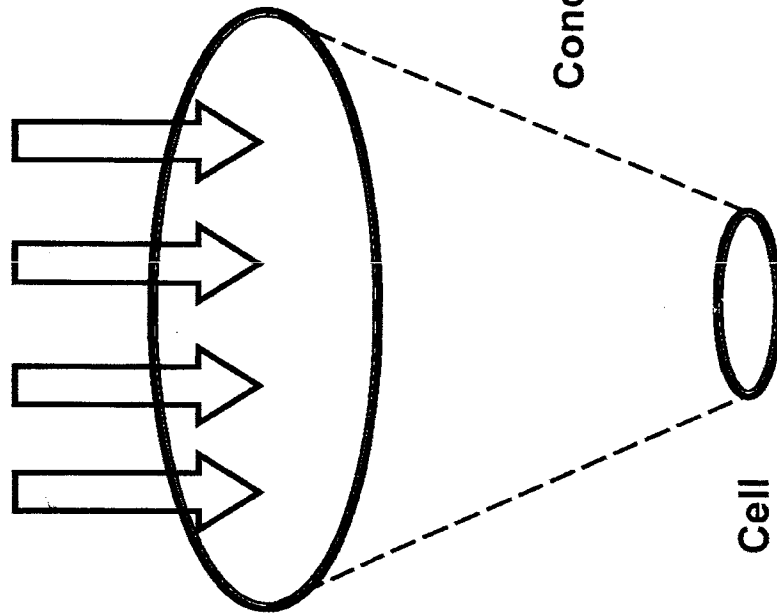
Peak plants	\$/kWh
Industrial cost	0.13
“Negative cost” for emissions	0.10
Total Cost	0.23

Grid connected PV plants	\$/kWh
Industrial cost	0.12-0.25
Stand alone PV plants	0.10-0.35
Diesel/PV hybrid	0.15-0.30

There Are Many Technology Candidates for Large-Scale PV Use in the Future



Sunlight



Lens

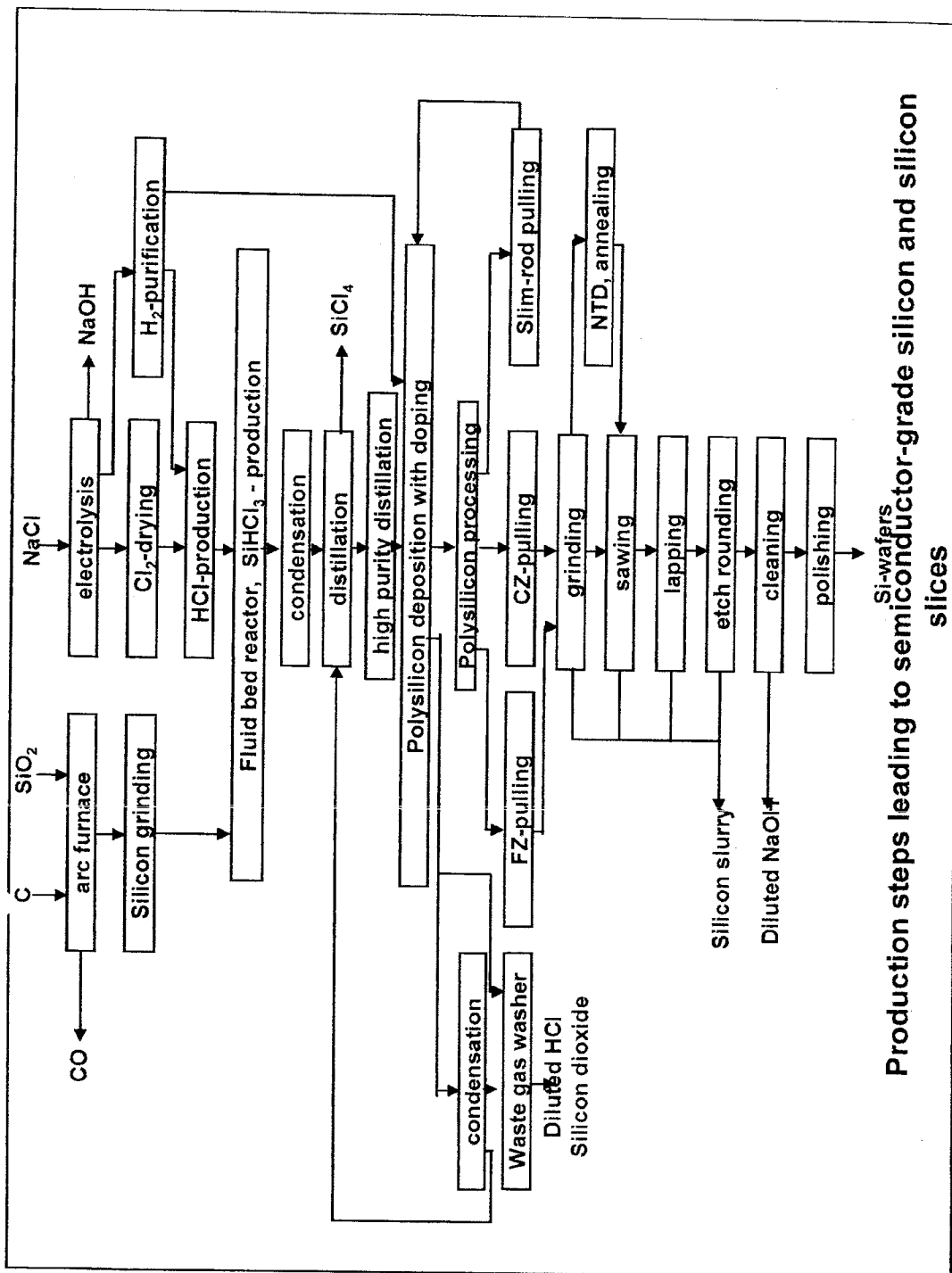
Cell

$$\text{Concentration ratio} = \frac{\text{Area of lens}}{\text{Area of cell}}$$

World PV Cell/Module Production (1988-2002) (in Megawatts)

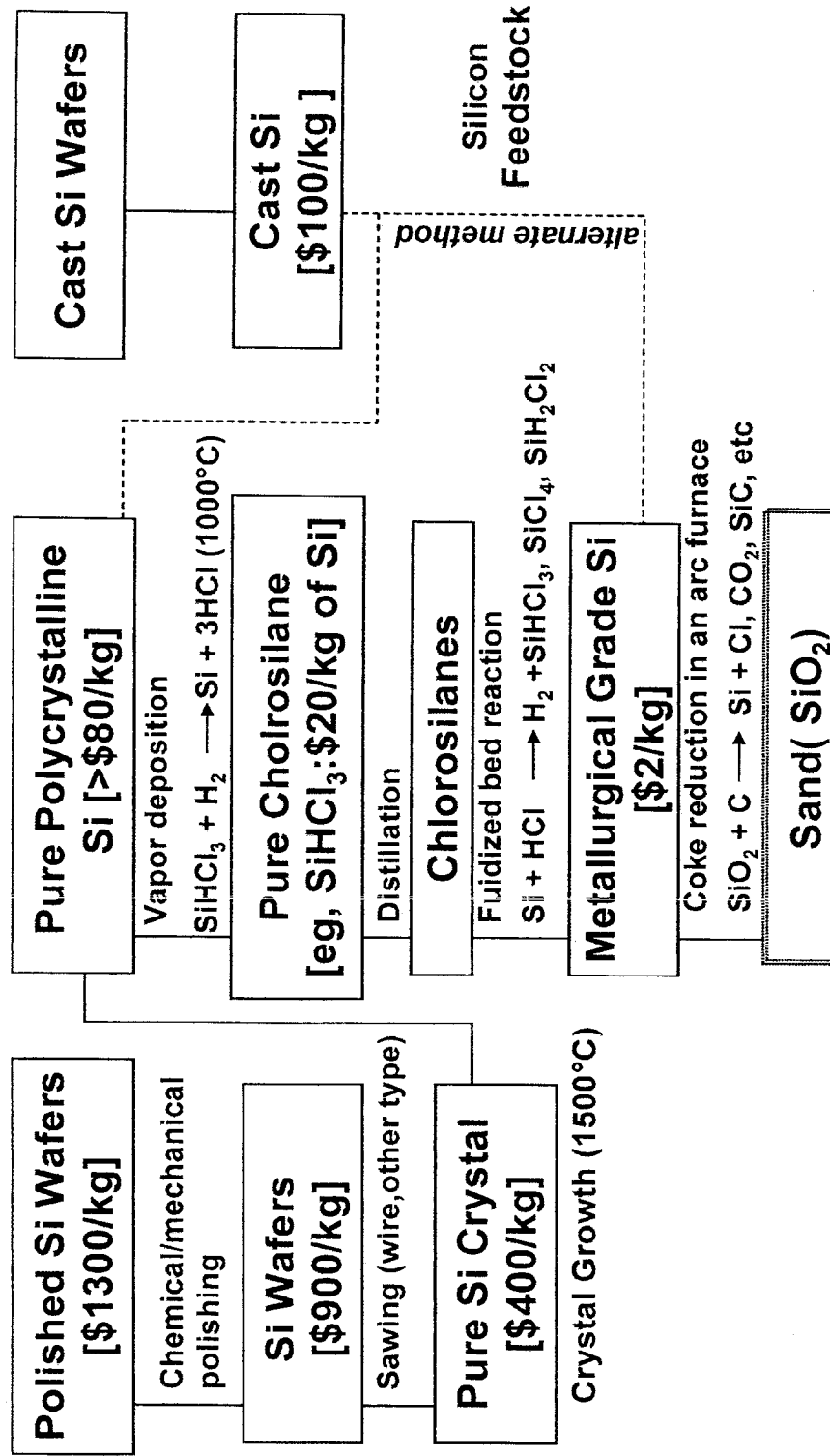
	1990	1991	1992	1993	1994	1995	1996
Rest of World	4.7	5	4.6	4.4	5.6	6.35	9.75
Europe	10.2	13.4	16.4	16.55	21.7	20.1	18.8
Japan	16.8	19.9	18.8	16.7	16.5	16.4	21.2
U.S.	14.8	17.1	18.1	22.44	25.64	34.75	38.85
Total	46.5	55.4	57.9	60.09	69.44	77.6	88.6

	1997	1998	1999	2000	2001	2002
Rest Of World	9.4	18.7	20.5	23.42	36	51
Europe	30.4	33.5	40	60.66	98	152
Japan	35	49	80	12.86	172	276
U.S.	51	53.7	60.8	74.97	94	142
Total	125.8	154.9	201.3	287.65	401	620

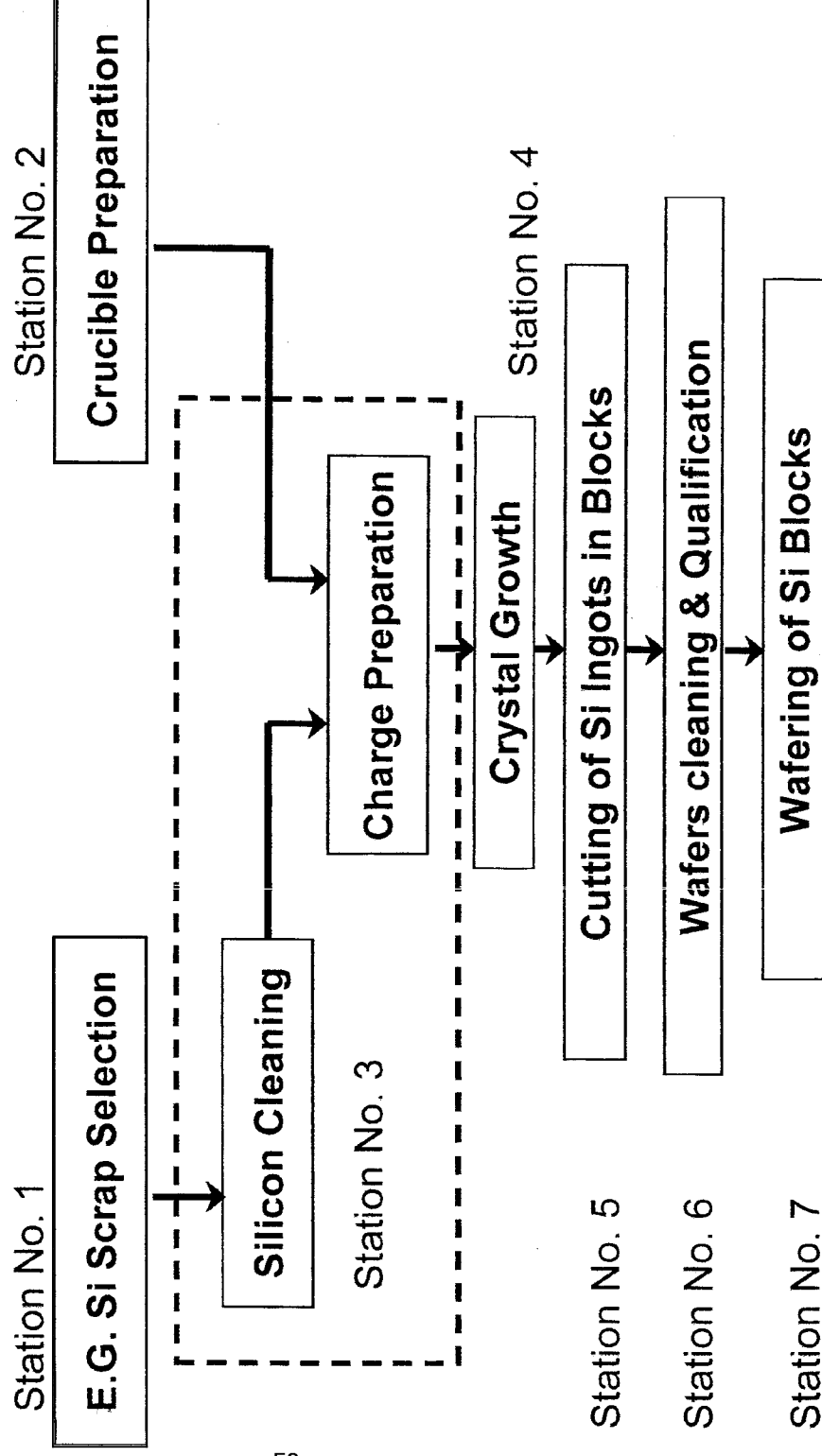


Production steps leading to semiconductor-grade silicon and silicon slices

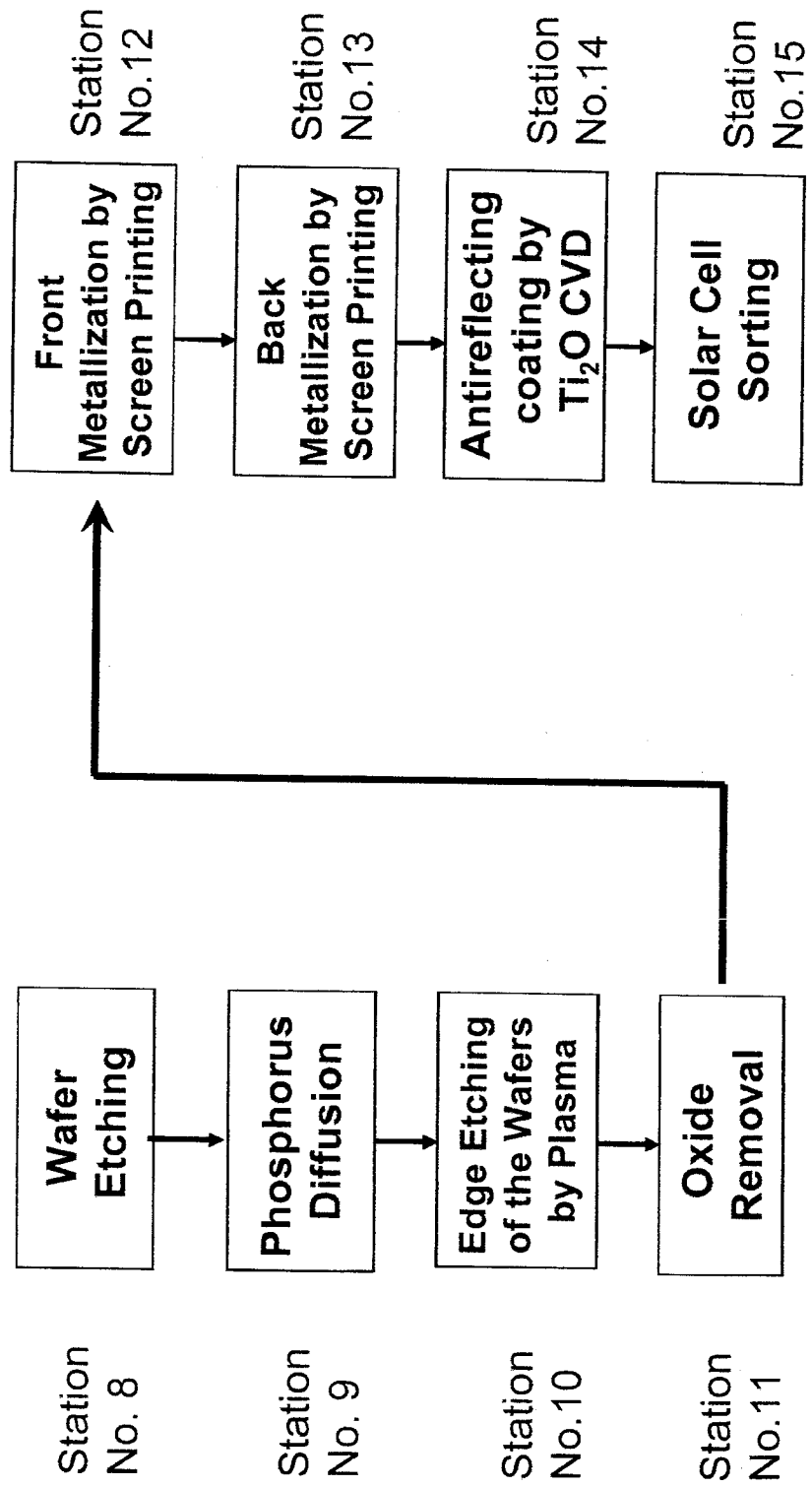
Silicon Process Steps



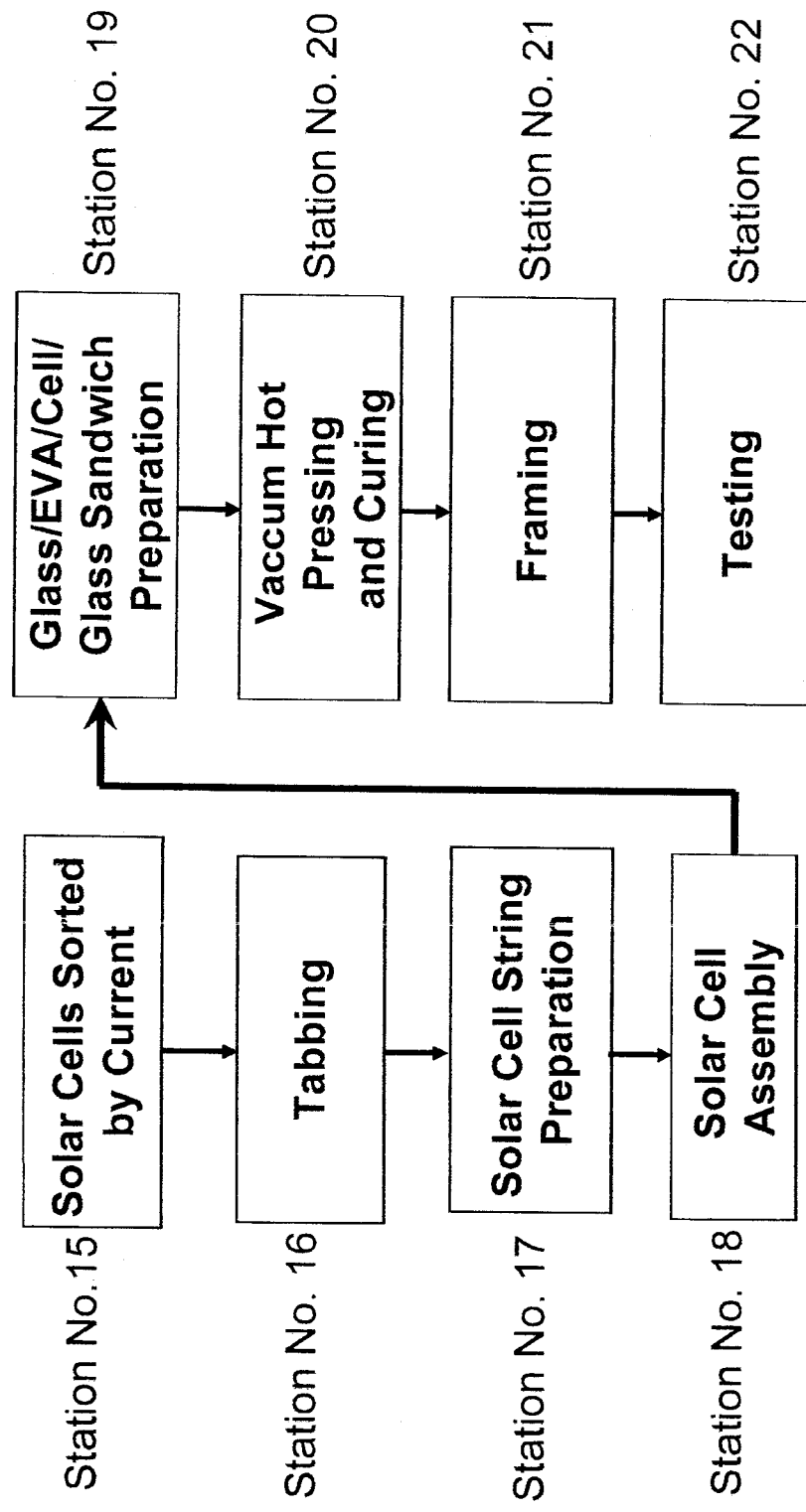
Crystal Growth & Wafering Line Process



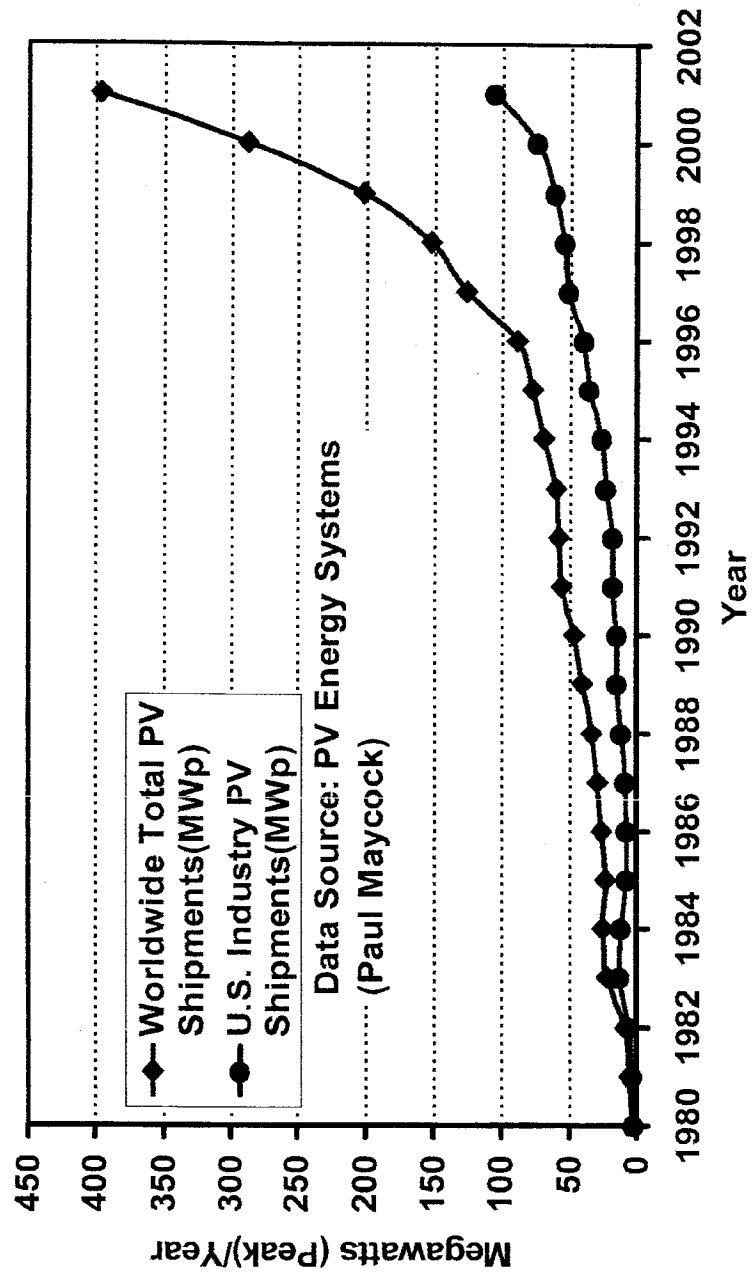
Solar Cells Production Process



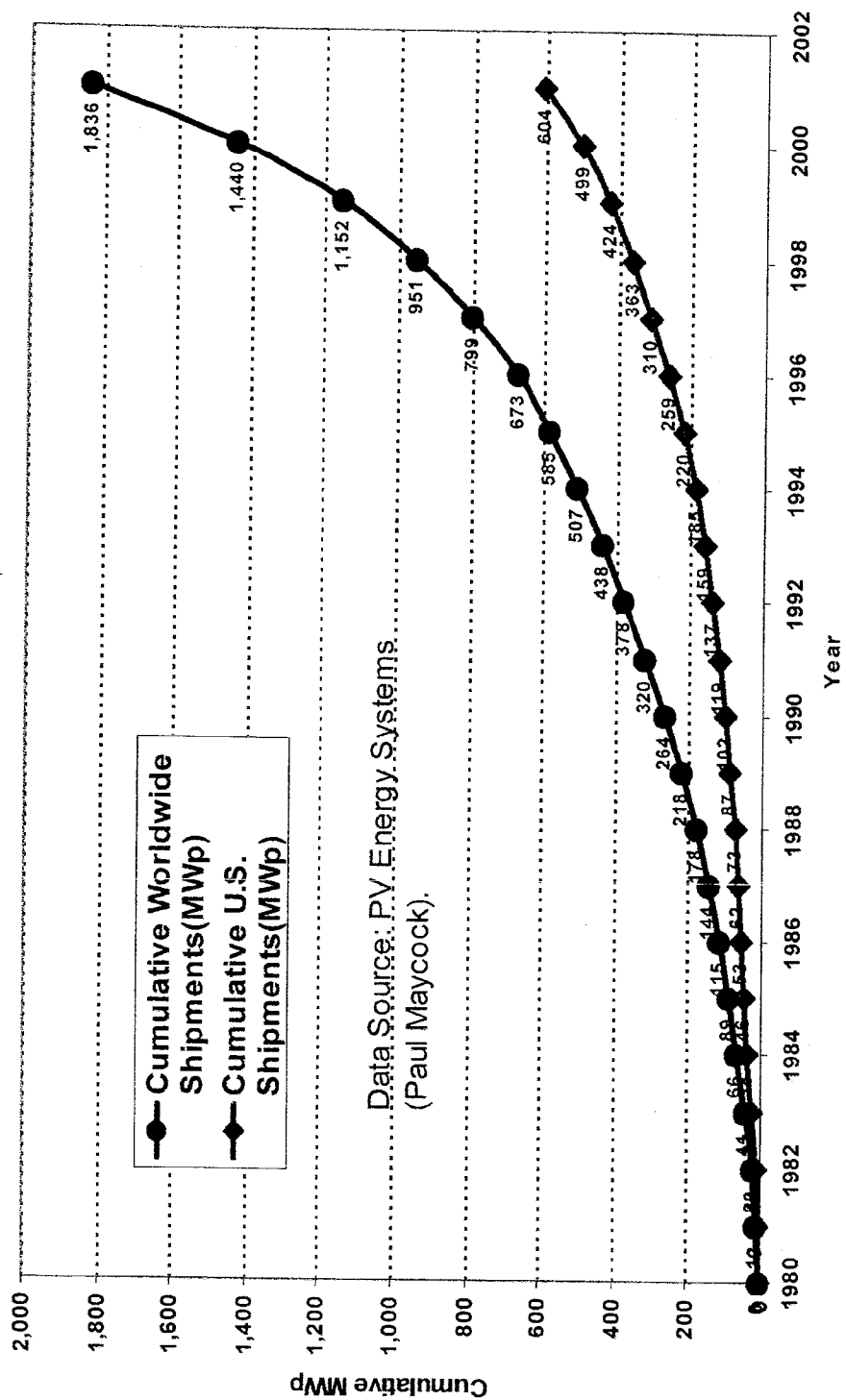
PV Module Assembling



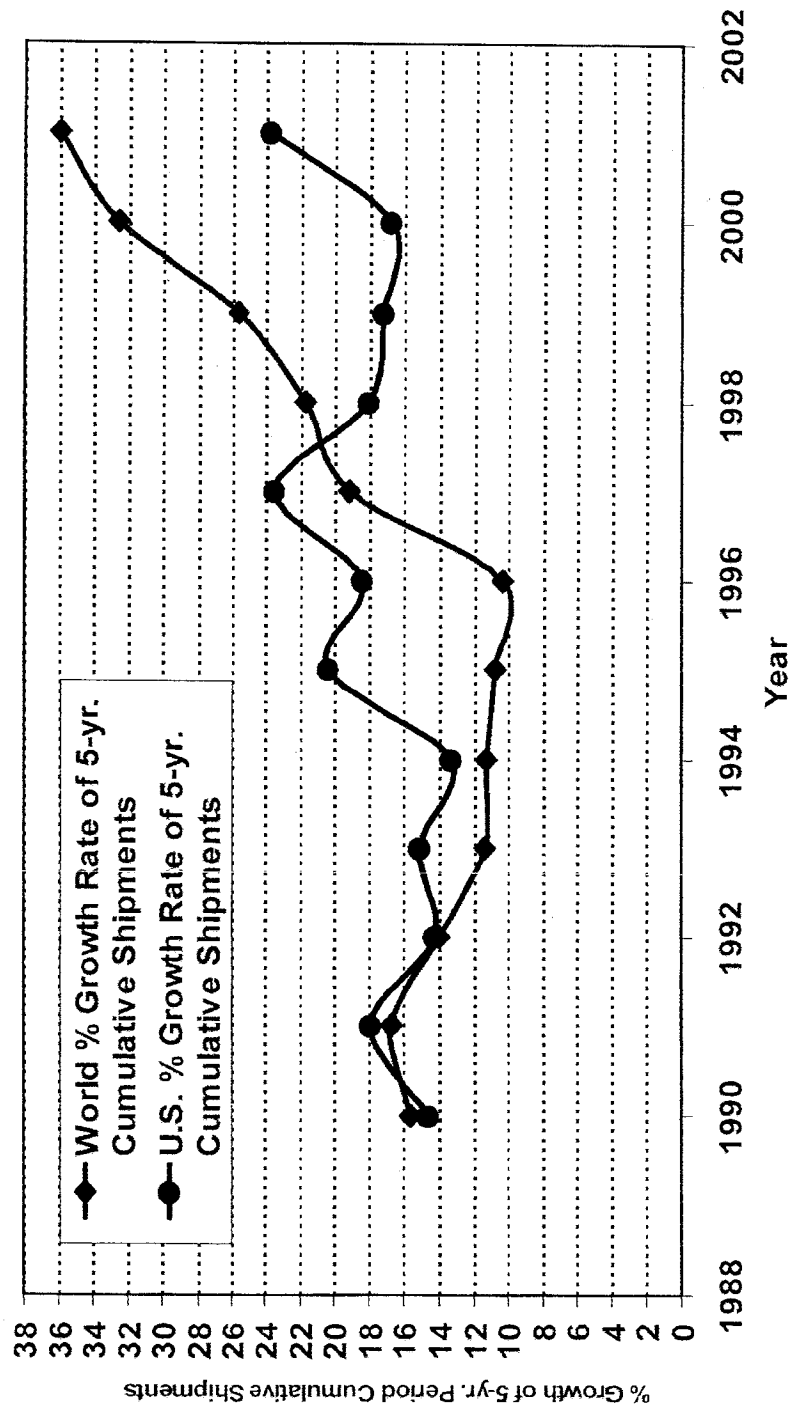
Comparison of U.S. and World Total PV Module Shipments



Comparison of Cumulative World Total vs U.S. Module Shipments



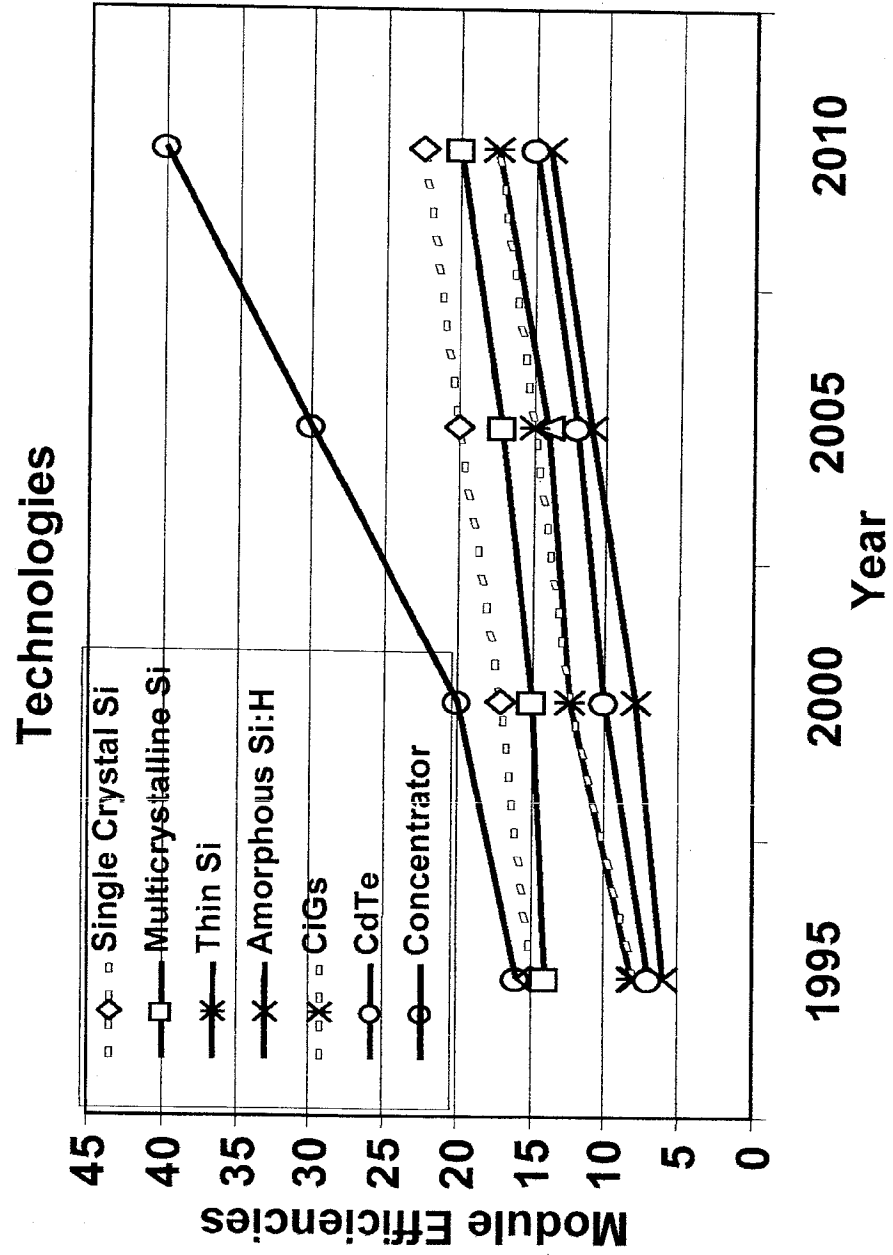
Comparison of U.S. and World 5-Yr. % Growth of Cumulative Shipments



Global Potential for Off-grid PV

Country	Population (millions)	Population Off-Grid (millions)	Potential PV Capacity (MW)
Africa (South of the Sahara)	310	280	14,000
Africa (North of the Sahara)	135	56	380
Asia (Southeast) and Oceania	520	375	26,600
Brazil	145	23	2300
China	1070	400	28,000
India	770	600	42,000
Indonesia	175	80	9800
Mexico	80	20	800
Russia	280	5	550
South and Central America (Spanish)	190	40	5250
South and Central Europe	195	15	1180

Module Performance: Status and Prediction for Various Technologies



Manufacturing cost of Terrestrial Modules

Option	1996 Price	1998 Price	2000 Cost/Price	2002 Cost/Price	2010 Cost/Price
Single Crystal	3.30/4.25	3.00/3.50	2.5/3.5	2.2/3.00	1.20/2.00
Polycrystal	3.20/4.25	2.80/3.20	2.5/3.5	2.2/3.00	1.20/2.00
Ribbon	/	3.0/3.5	2.5/3.5	2.2/3.00	1.20/2.00
Concentrator (module plus tracker					
motor/electronics)	4.00	3.0/4.0	2.8/3.5	2.2/2.8	1.0/1.6
Amorphous	3.00-3.50	3.0/3.5	3.0/3.5	2.8/3.5	0.75/1.25
Ti Spheral	/	3.50	/	/	/
CIS	/	4.00	4.00	3.0/3.5	0.75/1.25
CdTe	/	/	3.5/4.0	3.0/3.5	0.75/1.25

(1996\$) - 2010 forecast is the limit of technology

Photovoltaic Technology Issues

Crystalline Silicon Solar Cells

- Si feedstock: solar grade, electronic grade waste, competitiveness
- Manufacturing cost: continued investments are required to improve manufacturing methods in order to increase yield and production volume and to improve cell and module performance. Production cost is going down appreciably.
- Manufacturing capacity: increase in the production capacities of cells and modules as well as Si feedstock is a must to satisfy the increasing demand. (Gigawatts per year demand forecast for near term).
- R&D: device engineering and development, materials production, process improvement

Polysilicon Suppliers and Production

Supplier	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Hemlock	2,200	2,800	3,400	4,000	5,000	6,200	6,800	7,200	8,000	8,000
AsiMI	1,200	1,350	1,575	1,800	2,700	4,300	5,500	5,500	5,500	5,500
Wacker	2,030	2,400	2,400	2,570	3,000	3,650	4,700	5,000	5,500	5,500
Tokoyanna	1,700	1,700	2,000	3,000	3,300	3,300	3,300	4,800	4,800	4,800
MEMC-US	800	850	930	1,260	1,400	1,400	1,400	1,400	1,400	1,400
MEMC-Italy	600	605	720	950	1,100	1,100	1,100	1,100	1,100	1,100
MMC-Japan	1,000	1,000	1,000	1,200	1,400	1,400	1,400	1,400	1,400	1,400
MMC-USA					500	1,000	1,000	1,000	1,000	1,000
Other	400	400	500	600	600	600	600	600	600	600
Total (MT)	9,930	11,105	12,525	15,380	19,000	22,950	25,800	28,000	29,300	29,300

Estimated Polysilicon Production Levels from 2004 through 2010

Year	2004	2005	2006	2007	2008	2009	2010
Estimate (MT)	32,230	35,453	38,998	42,898	47,188	51,907	57,097

Concentrator Module Outlook

Factor	1995	1998	2000	2002	2010
Cell Efficiency (%)	24	26	27	30	35
Module Efficiency (%)	20	22	25	28	30
Warranty (yr.)	10	12	15	20	20
Manufactured cost (\$/WP)	5.00	3.00	2.80	2.2	1.00
Profitable Price (40% gpm)	7.00	4.00	3.50	2.8	1.67

* Includes pedestal/tracker

Amorphous Silicon Technology Forecast

Factor	1998	2000	2005	2010
Cell Efficiency (%)	5-7	8-10	12	14
Module Efficiency (%)	5	7-9	9	11
Area Yield (%)	80	90	95	98
Warranty (yr)	10	15	20	20
Manufactured Cost (\$/W _p)	3.00	2.00	1.50	0.75
Profitable Price	5.00	3.33	2.00	1.15

Photovoltaic Technology Issues

Amorphous Si Solar Cells

- Manufacturing cost: to date, production cost per watt exceeds the crystalline Si solar cell, and capital costs for module manufacturing facilities are relatively high and it will remain so until the technology gains higher acceptance.
- Manufacturing capacity: a-Si captured 9–11% of the total shipment in 1997. It is expected to do better as the performance improves.
- R&D: most of R&D efforts are focused on improving stability and reliability and consequently long term performance which will determine the future of the technology.

Photovoltaic Technology Issues

Polycrystalline Thin Films

Cadmium Telluride (CdTe)

- Manufacturing cost: several process with scale-up potential are considered for manufacturing CdTe modules. However, commercial large scale manufacturing has not been reached and no cost advantages over crystalline Si can be predicted.
- Manufacturing capacity: the industry is far from stabilization and expansion, production capacity is insignificant and limited to prototypes for industrial demonstrations.
- R&D: control and optimization of the CdS/CdTe interface; development of stable contacts to CdTe; understanding of some key processing issues including the CdCl₂ treatment and doping.

Photovoltaic Technology Issues

Polycrystalline Thin Films

$\text{CuInSe}_2/\text{CuInGaSe}_2$

- Manufacturing cost: The technology did not bridge the gap between costly prototype production procedures and large scale commercial production.
- Manufacturing capacity: There will be no significant production capacity until large scale, high yield industrial manufacturing procedures are established.
- R&D: Development of both front and back contacts and alternative window layer to replace CdS. Process development (less complex device structure); effect of molybdenum (Mo) on the cost of contact and the role played by sodium impurities related to electrooptical and structural characteristics.

Photovoltaic Technology Issues

Materials

- Manufacturing cost: cost of production of solar cells made of GaAs and other III-V materials is prohibitive for terrestrial applications.
- Manufacturing capacity: the production capacity is limited to space applications. Concentrators has a potential for small industrial base.
- R&D: recent R&D efforts have been devoted for polycrystalline III-V solar cells and new technologies (e.g. thermophotovoltaics).

**Microstructure Characterization of Thin Film Silicon and Related Materials
by Effusion of Implanted Rare Gas Atoms**

W. Beyer

**Institut für Photovoltaik, Forschungszentrum Jülich GmbH
D- 52425 Jülich, Germany**

Abstract

The article reviews shortly the application of thin film silicon, its preparation and some structural properties. The structural characterization of such materials by effusion measurements of implanted rare gases as well as of hydrogen is discussed in some detail.

1. Introduction

Thin film silicon is a class of material involving amorphous silicon, microcrystalline silicon as well as alloys of silicon with, e.g. carbon, nitrogen, oxygen, germanium. Usually, these materials contain hydrogen in the range of 5 to 15 at.% and, therefore, are termed a-Si:H, μ c-Si:H, a-Si:C:H etc. Thin film silicon is of considerable technological (and economic) interest. About 10 % of world solar cell production (about 250 MW in the year 2000) is made up of thin film (amorphous) silicon (the rest is single- and poly-crystalline Si). Thin film transistors (TFT) made of amorphous and crystallized silicon are widely used for large area liquid crystal displays in computers or television sets. Various other applications involving color sensors, position sensors, pressure sensors etc. are already produced. Although single-/poly-crystalline Si solar cells have higher efficiencies, thin film Si has some advantages: (1) an easy upscaling to large areas (much larger than typical single crystals) due to thin film deposition methods, (2) a high potential of cost reduction due to the use of only very thin (1 μ m) layers of semiconductor material which is deposited on cheap substrates like glass, plastics, stainless steel and (3) the possibility to vary the spectral sensitivity by using Si alloys with Ge or C/N/O with energy gaps between 1 eV and more than 2 eV. Thus, the application of thin film silicon may, e.g., decrease the costs of solar generated electricity. For these reasons, an intensive research is going on worldwide for a better understanding and a better control of these materials.

2 . Preparation of thin film silicon

Thin film silicon is predominantly prepared by plasma deposition; in recent time also hot wire deposition is applied. Fig. 1 shows the schematic setup of these methods. In both cases, the gas silane (SiH_4), typically at a pressure of 0.1 to 10 mbar, is decomposed and radicals, like SiH_3 , are formed. These radicals stick to the substrate and film growth proceeds by polymerization under release of H_2 . Doping is achieved by addition of gases like phosphine (PH_3) or diborane (B_2H_6). Additional flows of (e.g.) CH_4 , CO_2 , NH_3 and GeH_4 result in the growth of Si:C:H, Si:O:H, Si:N:H and Si:Ge:H alloys, respectively, and by dilution with H_2 microcrystalline material is obtained.

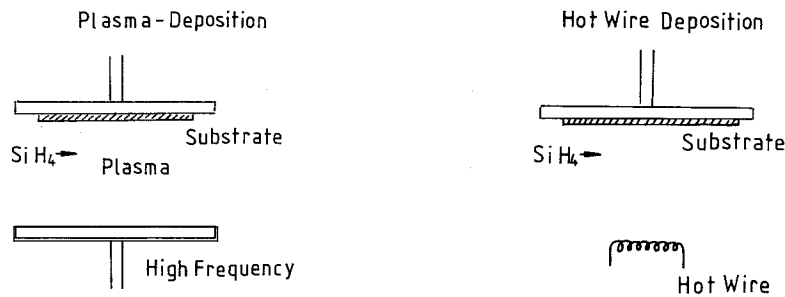


Fig. 1. Setup (schematic) for plasma and hot wire deposition

3. Material problems in thin film silicon technology

In particular for low cost solar cell production, low substrate temperatures (compatible with the use e.g. of plastic substrates) and high deposition rates (up to 10 Å/s or more) are required. Moreover, the use of a-Si alloys is expected to lead to higher solar cell efficiencies as a larger fraction of the solar spectrum may be utilized. In all these cases, material quality is presently limited by defects (mostly Si dangling bonds) related to microstructure. Films do not grow homogeneously but contain empty spaces (voids), as shown schematically in Fig. 2.

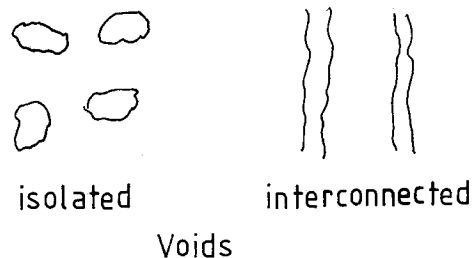


Fig. 2. Types of voids in thin film silicon

Voids lead to electronic defects mostly because hydrogen desorbs from void surfaces (during film deposition or thereafter) leaving behind dangling bonds or strained bonds.

4. Microstructure detection in thin film silicon

For microstructure detection, various methods have been applied, like:

- high resolution TEM
- small angle X-ray scattering
- IR absorption
- oxygen (water) penetration
- hydrogen effusion
- effusion of rare gases.

Aiming for methods to detect microstructure effects rapidly, we discuss in the following the latter two methods.

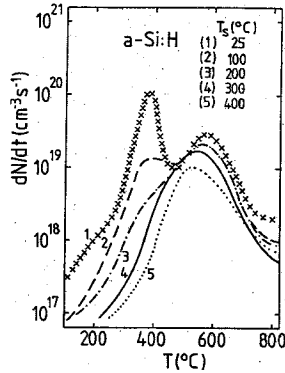


Fig. 3. Hydrogen effusion spectra of a-Si:H deposited at various substrate temperatures

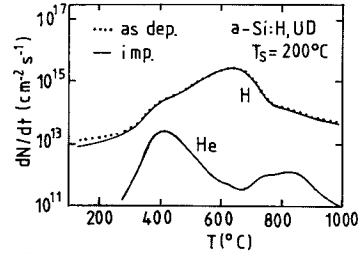


Fig. 4. Helium and hydrogen effusion spectra of a-Si:H deposited at $T_s = 200^\circ\text{C}$

5. Microstructure characterization of thin film Si by effusion of rare gases and of hydrogen

In case of H effusion, hydrogen incorporated in the material is used as a probe of microstructure. E.g., one can distinguish from the effusion spectra between diffusion of molecular (H_2) and atomic hydrogen. In case of rare gas (He, Ne, Ar) effusion one makes use of the fact that these gases do not form bonds to silicon. Therefore, rare gas effusion is expected to depend on network openings. Rare gases can be brought into the material during deposition or by ion implantation. Here we confine ourselves to implanted rare gases.

5.1 Experimental

Rare gas implantation was done at room temperature, using a mass separator. Implantation energy was 40 keV for He^+ , 100 keV for Ne^+ and 200 keV for Ar^+ resulting in depth distributions with maxima at the depth of 0.4 μm (He) and 0.2 μm (Ne and Ar) estimated by TRIM. The dose was 10^{16} cm^{-2} or less. A rather low dose is necessary to avoid implantation-related changes of the material structure. Effusion measurements were performed as reported elsewhere [1] with a heating rate of $20^\circ\text{C}/\text{min}$.

5.2 Results and Discussion

Typical results of hydrogen effusion measurements for (plasma-grown) a-Si:H are shown in Fig. 3. Plotted is the H effusion rate as a function of temperature. The spectra show two effusion peaks. The low temperature (LT) effusion peak is attributed to H_2 -outdiffusion from voids; the high temperature (HT) peak is attributed to H-outdiffusion from compact material. It is seen that with decreasing substrate temperature the hydrogen content increases, giving rise to a change from compact to void-rich material. Good quality material is prepared near $T = 200^\circ\text{C}$. This type of material will be (mainly) discussed in the following.

Fig. 4 shows typical results for the effusion of (implanted) helium from good-quality undoped (plasma-grown) a-Si:H. In the upper part, the hydrogen effusion is plotted showing a single (HT) effusion peak. The close agreement of H effusion prior to (dotted line) and after He implantation (full line) suggests that the material structure is only slightly changed by the He implantation process. He effusion (lower part) shows two effusion peaks. The LT peak is attributed to He out-diffusion from Si network and the HT peak attributed to He effusing from isolated voids in a permeation process.

For diffusion-limited effusion of H from a thin film, the solution of diffusion equation gives [2]

$$D/E_D = d^2 \beta / k \pi^2 T_M^2 \quad (1)$$

with the heating rate β , the film thickness d and the temperature T_M of the effusion maximum. Using Eq. (1), the helium diffusion energy E_D can be estimated assuming an Arrhenius dependence $D = D_0 \exp(-E_D/kT)$ and a diffusion prefactor of $D_0 = 10^{-3} \text{ cm}^2 \text{ s}^{-1}$.

As a result, we obtain from the data in Fig. 4 (LT He peak at $T_M \approx 400^\circ\text{C}$) a He diffusion activation energy of $E_D \approx 1.1 \text{ eV}$. This is in good agreement with literature data [3] for He diffusion in crystalline silicon (c-Si):

$$D = 0.11 \text{ cm}^2 \text{ s}^{-1} \exp(-1.25 \text{ eV}/kT).$$

For permeation of a gas through a solid, the relation $P = S D$ is valid, with S the solubility, P the permeability and D the diffusion coefficient [3]. Literature data for c-Si [3] give:

$$S = 6.5 \cdot 10^{14} \text{ cm}^{-3} \exp(-0.48 \text{ eV}/kT) p \text{ (pressure),}$$

$$P = 7.2 \cdot 10^{13} \text{ cm}^{-1} \text{ s}^{-1} \exp(-1.73 \text{ eV}/kT) p \text{ (pressure)}$$

As a consequence of the pressure-dependence, permeation will depend on void sizes and will occur at the higher temperature the bigger the voids or cavities are. In the following, we use the HT fraction of He effusion as a measure of the concentration of isolated voids.

Fig. 5 shows hydrogen and helium effusion spectra of undoped a-Si films deposited by various methods at a substrate temperature of 200°C . The methods were plasma-enhanced chemical vapor deposition (PECVD), hot wire (HW), DC sputtering (SP). Also shown are the results of (plasma-grown) microcrystalline Si (μc). The lack of (LT) hydrogen effusion indicates in all cases the lack of interconnected voids. It is seen that the HT part of He effusion, i.e. the concentration of isolated voids, depends significantly on the deposition process.

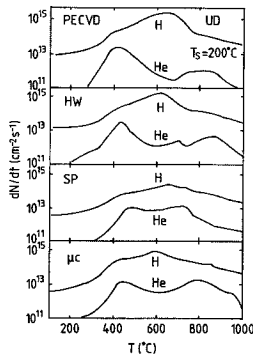


Fig. 5. Effusion of He and H for undoped Si:H deposited by various methods

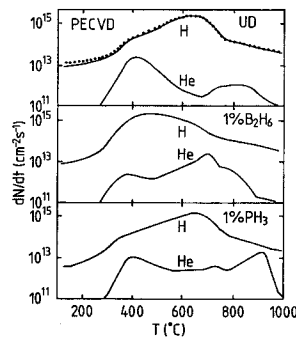


Fig. 6. Effusion of He and H for doped and undoped PECVD a-Si:H

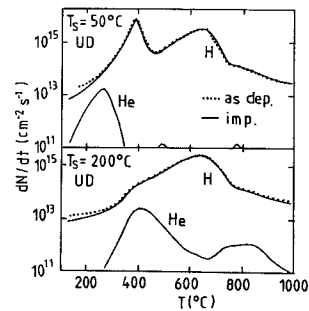


Fig. 7. Effusion of He and H for undoped PECVD a-Si:H deposited at different substrate temperatures T_s

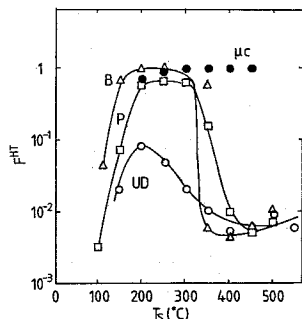


Fig. 8. HT fraction of He effusion versus substrate temperature T_s of PECVD a-Si:H (undoped (UD) and P and B doped) and of μ c-Si:H (μ c)

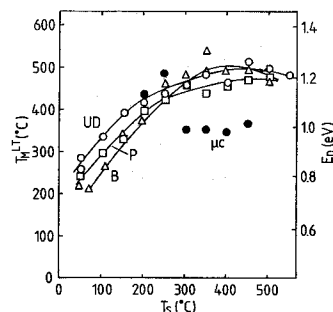


Fig. 9. Temperature T_M^{LT} of LT He effusion peak versus substrate temperature of PECVD a-Si:H (undoped and P and B-doped) and of μ c-Si:H (μ c))

Fig. 6 demonstrates that the HT part of He effusion depends also on doping. Shown are effusion spectra of (PECVD) a-Si:H, undoped and doped with 1% diborane and 1% phosphine. Doping is found to increase significantly the HT He effusion, i.e. the concentration of isolated voids.

The effect of a decrease in substrate temperature for (undoped) plasma-grown a-Si:H is demonstrated in Fig. 7. For a substrate temperature of 50°C, the presence of a LT hydrogen effusion peak shows that this material has interconnected voids. He effusion shows only a LT effusion peak which is at lower temperature than in more dense $T_s = 200^\circ\text{C}$ reference material. The lack of HT He effusion, i.e. of isolated voids, is attributed to the presence of interconnected voids.

Fig. 8 shows the fraction F^{HT} of high temperature He effusion for plasma-grown doped and undoped a-Si:H as well as for μ c-Si:H (undoped) as a function of substrate temperature. While the decrease of F^{HT} at low substrate temperatures is attributed to the presence of interconnected voids, the decrease of F^{HT} at high temperatures in case of a-Si:H suggests a role of hydrogen in the formation of isolated voids, as the decrease of F^{HT} coincides with a decrease in H concentration below 3-5 at.%. For μ c-Si:H, the high value of F^{HT} , i.e. the high density of isolated voids, is attributed to the presence of grain boundaries.

The influence of the substrate temperature on the LT He effusion temperature and the He diffusion energy (determined by eq. 1) in plasma-grown a-Si:H and μ c-Si:H films is shown in Fig. 9. It is seen that with decreasing substrate temperature (increasing hydrogen content) T_M^{LT} and the He diffusion energy drop for a-Si:H in agreement with the decreased material density. Doping affects these parameters only slightly.

In Fig. 10, the dependence of T_M for implanted He, Ne and Ar on alloy concentration is demonstrated for a-Si:O:H alloys [4]. For all three atomic species, T_M is found to decrease in agreement with a decrease in material density. The drop in the hydrogen effusion temperature (dotted line) at about 20 at.% O indicates the change of H diffusion from diffusion by atoms (at low O concentration) to diffusion by molecules. Qualitatively, the different effusion

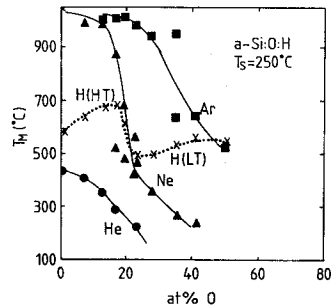


Fig. 10. Temperature T_M of (LT) He, Ne and Ar effusion peaks as well as of hydrogen effusion maxima for a-Si:O:H alloys of various composition

temperatures of the rare gases can be explained in terms of "doorway" diffusion process [5] by an influence of the atomic radius on the diffusion energy. According to Anderson and Stuart [4] the relation

$$E_D = 4 \pi G r_D (r - r_D)^2 \quad (2)$$

is valid for doorway diffusion with r the radius of the diffusing atom, r_D the doorway radius and G the shear modulus of the material. According to this formula, however, the exact size of network openings is not obtained by effusion experiments. Rather information is obtained on the stability/motion of molecules of certain sizes at certain temperatures. By comparison, the stability of other molecules (like, e.g. of H_2O or of H_2) can be predicted.

6. Conclusions

Effusion of rare gas atoms (and hydrogen) is found to be a useful method for microstructure characterization of thin film silicon. The results reveal microstructural properties which are rather sensitive to preparation method, doping, substrate temperature and alloying. Being a relatively fast method, the technique can contribute to a better control of thin film silicon, a material of considerable technological importance. The technique may also be useful for microstructure characterization of other thin film materials.

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2. W. Beyer, in: Tetrahedrally Bonded Amorphous Semiconductors, D. Adler and H. Fritzsche, eds. (Plenum Press, New York, 1985) p. 129
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4. W. Beyer and F. Finger, Mater. Res. Soc. Symp. Proc. 715 (2002) A5.1
5. O.L. Anderson and D.A. Stuart, J. Am. Ceram. Soc. 37 (1954) 573

Research Activity in the Solar Cell Laboratory
Institute of Graduate Studies and Research
Alexandria University

Moataz Soliman
Materials Science Department
Institute of Graduate Studies and Research
Alexandria University
163 Horrya Avenue, PO Box 832
Alexandria, Egypt
Email:msoliman2@yahoo.com

This Laboratory is the best-equipped laboratory all over the country for doing research in the field of solar cells. The laboratory had been supported by:

A-UNESCO

B-Joint project between Alexandria University and Eindhoven University to transfer the *Technology of Solar Cells*.

We have an interest in solar energy because:

- 1- We have areas in Egypt with the highest solar insolation all over the world,
- 2- We have many scattered areas that are far from the utility grid, and the solar energy will be the proper source in order to reclaim these areas and eventually redistribute the Egyptian population (95% of the population occupies only 5% of the land),
- 3- We have now a great concern about our air quality and the effect of conventional energy sources, so we should increase the use of renewable energy sources.

Available Equipment

A-Cleaning

- 1- Deionizing Unit
- 2- Distillation Unit
Double distiller
- 3- Chemical Hod
(FISHER)
- 4- Magnetic Stirrer and Hot Plate
Up to 1100 r.p.m, $T_{\max} = 350^{\circ}\text{C}$
- 5- Oven
(Heraeus) up to 250°C
- 6- Conductivity Meter
(Jen Way) PC M3

B-Diffusion

- 1- Diffusion Furnace
(Thermoco), three quartz tubes diameter 10.4 cm, Temp. up to 1300°C , Quartz Boot with 25 slots
- 2- Flow Meters
(Brooks) from 0.05 to 4.7 LPM
- 3- Thermocouples
- 4- Photoresist Spinner
(Head Way Research)
- 5- Timer/Tachometer
(Head Way Research)
- 6- Speed Control
(Minarik)
- 7- Wafer to Mask Alignment and Exposure System
(Cobilt)
- 8- Automatic Angle Lapping Machine
(Signatone)
- 9- Sterozoom Microscope
(Bausch & Lomb)
- 10- Four Point Probe System
(Signatone)

C-Evaporation

- 1- Vacuum Coating Machine
(Edward) up to 7×10^{-7} mbar, two filaments
- 2- FTM 5 Thickness Monitor
(Edward) 0.0nm to 999.9 micron

- 3- Mechanical Masks
Four masks for the front metallization

C-Cell Testing

- 1- XYT Recorder
ZSKT (Rohd & Schwarz)
- 2- Power Supplies
(Delta Elektronika)
- 3- Standard Solar Cell
(Solarex) AM1 & AM0
- 4- Tungsten Halogen lamps
1000W
- 5- Lux Meter
(Traceable), three ranges
- 6- Light Meters
(Spectra-Physics) 404 ,micro watts to 5watts
- 7- Electrometer
(Keithly) 602
- 8- Optical Filters
(Balzers) 20 Filters

D-Encapsulation

Home Made Panel Assembly Unit

The staff doing the research in the laboratory is eight members. The group leader is Dr. Prof. Mahmoud Shabana.

The current research areas are:

- 1- *Fabrication and characterization of p-n junction silicon solar cells by diffusion process using spin on sources,
Thickening of grid fingers using electrochemical deposition
- 2- Fabrication and characterization of MIS solar cells,
Effects of oxidation time and temperature on the cell performance
- 3- *Studying the effects of illumination, heating and radiation on the MIS solar cells,
Effects of these parameters on the cell performance

- 4- Modeling of MIS/IL solar cells,
Effects of fabrication parameters on the cell performance
- 5- Preparation of metal oxide using spraying technique,
Effects of solution parameters and substrate temperature
- 6- *Fabrication of CdS/CdTe/ZnTe/C heterojunction solar cells using
electrochemical deposition technique,
Effects of solutions parameters, temperature, addition of copper, and heat
treatment on the cell performance
- 7- *Preparation of selective coating for flat plate collector
Effect of preparation parameters of electrochemical deposition on the
selectivity of flat plate collector
- 8- *Fabrication of dye sensitized nano structured solar cells
Preparation of nano structured ZnO using electrochemical deposition,
and effect of particle size of TiO₂ on cell performance.

We are looking for joint projects to keep on doing research in the
field of Photovoltaic energy

Areas for joint projects:

- 1- Research projects within the above research topics, field studies,
system performance, and preparing educational kits for students,
- 2- Workshops and training courses,
- 3- Exchange of visiting staff members.

Photovoltaics Applications and Research in Egypt

Said H. EL-Hefnawi

**Photovoltaic Cells Department, Electronics Research Institute,
NRC Building, Tahrir Street, Dokki, Cairo, Egypt,
Tel: 202-3310510, Fax: 202-3351631,
Email: shfnawi@hotmail.com**

ABSTRACT

Egypt is one of the countries, which has favorable solar energy conditions and good potential for solar energy utilization. The majority of Egypt's population is living in only 6% of the land, with the remaining 94% of the land as desert. A national program to develop renewable energy systems was started in 1957 in National Research Center of Egypt. Since then many academic institutions have been involved in academic research on different aspects of solar cell technology.

The interest in renewable energy sources started with a promotion for replacing the depleting commercial sources but now the interest has taken a more important dimension that renewable energy sources are clean sources with no harmful effect on the environment.

This paper discusses the different photovoltaic activities and projects in Egypt with emphasis on community field projects utilizing PV for different applications. There are four main field studies addressing integrated approach to rural community development. Lessons learned and recommendations from the field experiences are summarized.

This paper also introduces the recent activities, including internal and external projects, of Photovoltaic Cells Department (Electronics Research Institute) in the fields of monocrystalline silicon solar cells preparation, thin films, and applications.

INTRODUCTION

Despite the internal migration of rural people to urban areas, around 4 billion people still live in rural areas of developing countries and most of them with little or no access to electricity. Only, in few cases, electric power is produced by stand-alone generator sets. Social life in the evenings is usually extended for a couple of hours by a kerosene lamp. What is common to all, however, is that sunrise and sunset still mark the beginning and end of every day. It is widely accepted that electricity still spurs the social and economic development of rural areas. Availability of electric power is decisive for the supply of good drinking water, the conservation of food, the storage of medical supplies, radio, TV, telecommunication, etc.

It is also obvious that along the anticipated path for development, many developing countries will increase their energy consumption, a large portion of which will be covered by conventional sources like oil, gas and coal. This will undoubtedly contribute to an increase in the world's carbon-dioxide (CO₂) production. Solar technology has the advantage of being one the very few CO₂-free energy converting technologies.

It was after the so-called energy crises of the Seventies that the interest and focus on renewable energy sources of energy. Particularly, solar energy had jumped upward almost overnight and that interest kept increasing over the years. Solar energy is divided into two main categories: solar-thermal and photovoltaic. While solar-thermal is self-explanatory, PV is a special technical term uncommonly recognized by the layman particularly in developing countries. PV is simply a technology that converts light into electricity, irrespective of the source of light. However, there are many PV materials and devices, and their design, fabrication, and performance vary a great deal from one PV material to another and from one cell design to another.

Photovoltaic have been shown to offer many advantages:

- PV systems do not need fuels; in remote areas of developing countries in particular, diesel or kerosene fuel supplies are unreliable and expensive.
- PV systems are modular; therefore, an array which is composed of several modules can be tailored to size to meet a particular load.
- PV systems are highly reliable as compared to those of diesel generators.
- PV systems are easy to maintain compared to alternative technologies.
- PV modules have long lifetime with little degradation in performance over 20 years.
- PV systems are environmentally benign causing no pollution and no contribution to global warming.
- PV systems have proven recently to be economically viable for small-scale applications as compared with diesel systems or other small power supplies.
- PV systems can improve the quality of life, for instance, lighting in a rural school, refrigeration of vaccines at a rural clinic or powering a radio transceiver or a TV in a remote location.

Applications of photovoltaic cover a wide range covering almost every aspect of rural activities. Examples are:

- Rural electrification,
- Water pumping and treatment systems,
- Health care systems,
- Communications,
- Transport aids like road signs and hazard signals,
- Security systems,
- Corrosion protection systems,
- Miscellaneous like consumer devices, feeding systems on fish farms, aeration systems in stagnant lakes, earthquake monitoring systems, fountains and emergency power for disaster relief,
- Income generating activities like battery charging, TV and video pay stations, village industry power and refrigeration services.

Egypt is one of the countries, which has favorable solar energy conditions and good potential for solar energy utilization. The amount of solar energy incidence per square meter varies between 5 and 8 kWh per day with duration of 3000-4000 hours per year. The majority of Egypt's population (60 million people in 1999) is living in only 6% of the land, with the remaining 94% of the land as desert. A national program to develop renewable energy systems was started in 1957 in National Research Center of Egypt. Since then many academic institutions have been involved in academic research on different aspects of solar cell technology. Few institutions have been involved in field applications of PV systems for community development. The potential for practical use of PV power was first tested in the field of Basaisa Village [1] in (Al-Sharkiya Governorate) in Sept. 1977. A solar module (18-watt peak) was used to power a 12-inch black and white communal TV set which was installed in the common hall „Mandara“ of Basaisa.

The interest in renewable energy sources started with a promotion for replacing the depleting commercial sources but now the interest has taken a more important dimension that renewable energy sources are clean sources with no harmful effect on the environment. The theme of the first World Renewable Energy Congress held at Reading, U.K., Sept. 1990 was taken as Energy and Environment into the 1990s. Less than two months after, the second International Symposium on Renewable Energy was held in Cairo (Oct. 1-4, 1990). About 150 research papers from 30 countries were presented during 24 sessions during the symposium. The general message was clean energy for better environment.

PHOTOVOLTAICS AND COMMUNITY DEVELOPMENT

The relationship between energy and community development is a dynamic one, in which the amount, type and quality of economic growth are mutually dependent variables on the quantity, kind and price of energy available. There is a growing consensus that successful

development requires a firm agricultural foundation, that the basic quality of life must be improved for and with the active participation of the poor majority of the population living in the countryside. Collective PV power systems for the thousands of small village communities and new desert settlements can be an attractive approach to successful community development in rural areas of the developing nations. If this can be done (no one suggests that it can be done either easily or quickly) then the rural poor may have reason and ability to reduce their birth rates, increase their production, and may no longer be migrate to already overcrowded towns and cities. The present vicious circle of over-populations, over-consumption of fuel, low-productivity of land and labor, health and economic hazards makes meetings even existing hazards energy needs a considerable task. Installation of PV power systems is but means for rural community development not the end in itself. Table 1 shows [2] a list of PV applications in Egypt as of 1999 with their location and source of funding.

There are four main field studies addressing integrated approach to rural community development. The Desert Development Center at Sadat City, Basaisa project in Al-Sharkiya Governorate, both sponsored by The American University in Cairo (AUC); the project at Meet Abou-El Kom village, in Al-Menoufia Governorate, which is sponsored by the National Research Center (NRC), and the pumping system at Nobareya area, which is sponsored by Germany. All four projects have used photovoltaics for different applications.

Desert Development Center

Two photovoltaic systems were installed in the summer of 1981. These are a 10 kW peak system, which through an inverter provides the 220V, 50 Hz, necessary to power the center's headquarter building as well as an AC submersible pump at Sadat City. In addition, a 3 kW peak DC system exclusively devoted to power a deep (42 meters) well pump as well as a booster pump for irrigation. Field testing of these systems, monitoring their performance and demonstrating their feasibility has been a major activity of the energy group of the center.

AUC-Basaisa Village Integrated Field Project

Small PV system were introduced as response to village expressed needs during long dialogues and discussions that took place in the common hall „Mandara“ of the village, between the project team and village inhabitants. The systems included: light for training and education classes, TV for community club, radio recorder, slide projector, loudspeaker for the mosque, portable and fixed irrigation pumps, PV powered video training system and lately a medical refrigerator.

Introduced as communal systems, it did not cater to the more wealthy villagers. All villagers become members of a newly formed community cooperative for development at Basaisa with each person paying one Egyptian pound a year as membership fee. They also contribute shares to the production section of the cooperative. Each collective project must have a local responsible person. The responsible persons were trained (through intensive training courses offered on-site for specific purposes) to install, operate, maintain and repair the technical systems as well as assist the project team in collecting data and record keeping.

In case of actual breakdown of a system or one component their first resource is to try to fix it themselves and only when that proves impossible, does the project team intervene and help. Costs of repair and maintenance as well as the incentives given to the responsible persons are paid from the cooperative budget. Light was used for training on income generating activities like knitting, dressmaking and handicrafts and as emergency light for such activities in case of electricity cutoff.

Meet Abou-El-Kom Village Project

The late president of Egypt Mohamed Anwar EL-Sadat (in his village) supported this project. PV systems include:

- (1) Loudspeaker for the mosque 280 W peak, introduced in Aug. 1979.
- (2) 1.47 kW peak for two medical refrigerators in the village health clinic introduced in 1981.
- (3) PV array (170 W peak) for colored TV in the Youth club in the village installed in 1982.

Table 1. List of PV applications in Egypt

Application	Size kW (peak)	PV Supplier	Location	Funding Source
Pumping				
Water lifting with instru- mentaion monitoring.	3	Arco Solar	Sadat City	World Bank & UNDP
Water lifting.	3	Lucas	East Oweinat	Italy
Water lifting.	18	Solarex	East Oweinat	Italy
Pumping & lighting.	28	Under study	To come	U.S. AID
Irrigation pump.	1.85	A.E.G	Mansoura	
Water lifting.	25-30	A.E.G.	Wadi Elnatron	Germany
Irrigation pumps.	0.24	Solarex	Basaisa	AUC-NSF
Portable pumping system	2.20	Siemens	Nobareya	DLR
4 Pumping units	18	Siemens	Wadi Elnatron	Germany
Telecommunication				
7 Telecommunication Systems.	0.24 (each)	BP Solar	Hurgada, Abu- Ghossoun, Matrouh, Siwa	UN/ UNDP
Radio communication	1	Solavolt	EL-Gara Petroleum Co. West. Desert	Petroleum Co.
Desalination				
Sea water desalination.	8.3	A.E.G.	Abu-Ghossoun	UN/UNDP
Desalination system.	28-30	Under study	To come	U.S. AID
Water purification system.	7	A.E.G.	High Tension Laboratory	Germany
Refrigerators				
29 lit. Vaccine fridge.	0.24	BP Solar	Cairo	UN/UNDP
10 lit. Vaccine fridge + colored TV + Loudspeaker amplifier.	2	A.E.G.	Meet Abu El- Kom	Germany
Ten 100 lit. Fridge & ten stabilizers.	3.6	Solarex	To come	UN/UNDP
Icemaker vaccine refregir.	0.50	Sensor Tech	Basaisa	AUC-NASA
Ice-maker	35	Bid eleva- tion stage	Wadi ElRayan (El-Fayoum)	U.S.AID
Others				
Power generation.	10	Arco	Sadat City	World Bank
Solar powered comm. TV.	32	Philips	Basaisa	AUC-NSF
Solar powered comm. video	100	Solarex	Basaisa	ADF
PV/Wind/Diesel hybrid	200	Pragma	East Oweinat	UNDP, Italy
Navigation alarm.	0.86	A.E.G.	Lake Naser	Germany
Battery charger.	0.11	A.E.G.	Mansoura	Germany
Microwave repeater.	27	A.E.G.	To come	Germany
Traffic control.	1.5	A.E.G.	Wadi Natron	Germany
Two air-traffic stations.	66	Solarex	Ismailia, El Saff, Helwan	U.S.AID
24 Repeat stations.	120	Solarex	Sinai	U.S.AID

20 Units for cathodic Protection.	4	Arco	Petroleum Pipes.	U.S.AID
650 Navigational buoys.	13	Solarex	Suez Canal	U.S.AID
20 Units for home lighting	4.24	Siemens	Wadi Elnatron	Germany
10 Units for street lighting	1	Siemens	Wadi Elnatron	Germany
15 Units for street lighting	1.5	Siemens	Zafrana	Germany

Nobareya Pumping Project

Within the frame of the Egyptian-German cooperation (represented by the New and Renewable Energy Authority (NREA) of Ministry of Electricity and Energy and the Deutsche Forschungsanstalt für Luft und Raumfahrt (DLR) of the Ministry of Research and Technology (MBFT)) a portable photovoltaic water pumping testing unit has been installed at west Nobareya (130 km from Cairo) to drip irrigate an area of 3 feddans. The main components of the unit are:

- (1) Steel container, which holds the unit component whenever, needed to be transported.
- (2) 62 monocrystalline Siemens solar modules, each 38 W_p.
- (3) Pressurized tank.
- (4) Deep well pump and surface pump 1.1 kW each.
- (5) DC-AC inverter.
- (6) Weather station.
- (7) Data Acquisition System (DAS).
- (8) PC connected to DAS to store and display the received data instantaneously, daily or monthly values and trace curves whenever needed.
- (9) Two batteries to ensure computer continuous operation through small inverter.

DEMONSTRATION SYSTEMS AT EREDO [2]

At the Egyptian Renewable Energy Organization (EREDO) installed three systems:

PV Powered AC Household Electrification System 3 kW_p

The objective of this system is to demonstrate the use of PV power in household electrification system in two different modes:

(a) Stand alone mode feeding AC loads

The storage system consists of 60 lead acid batteries. Each battery has an operating voltage of 2V and has a capacity of 260Ah. The system control includes some safety features, surge current protection, etc. The temperature compensated charge regulation unit is the main component of the system control. It has the function of controlling the current flow to the battery and to the loads according to the state of charge of the battery itself. Avoiding deep discharge and overcharge, the battery life is extended up to the predicted time. The system is equipped with a stand-alone inverter, which converts direct current (DC) into a true sine wave output voltage with very low harmonic distortion at high efficiency values. The efficiency of the inverter ranges between 85-90% at an output power of 10-100% nominal power. The loads of the system are: 5 lamps, 18 W each; 2 cooking stove, 1 kW each; vaccine refrigerator; drilling machine; refrigerator; television and radio.

(Two) Grid connection mode

The system is equipped with a grid-connected inverter that provides a true sine wave output voltage with very low harmonic distortion at high efficiency values and a powerful protection/interface control to the grid. The PV array system includes 60 monocrystalline modules 50 W_p each, and an average efficiency of 10.9%. The system is connected as 6 strings, 10 modules/string. All the data collection and efficiency calculations are done via data and PC, with probes reading all the desired parameters.

PV powered DC household electrification system 500 W_p

This system demonstrates the use of PV power in household electrification system working at stand-alone conditions and a system operating voltage of 24V. The system includes 12 monocrystalline PV modules; 45 W_p each and an average efficiency of 10.9%. The PV system is electrically connected as 6 strings, 2 modules/string. For any household system, a storage system is needed to supply power to the loads at night. 12 lead acid batteries are used. Each battery has an operating voltage of 2V and has the capacity of 25Ah. The system control includes some safety features, surge current protection, etc. The temperature compensated charge regulation unit is the main component of the system control. The system feeds the following DC loads: refrigerator 50 litres; 4 fluorescent lamps 11W each; 4 fluorescent lamps 18W each; 4 fluorescent lamps 36W each and 2 rheostats.

PV pumping system 1500 W_p

The objective of this system is to monitor the performance of submersible pumps using a closed loop hydraulic system. The system feeds a submersible electric water pump with an AC motor, which pumps the water to a 1m³ storage tank. The tank is equipped with all the meters needed to measure the flow and pressure. It also contains a control valve that takes its control signal from the pump inverter/controller. The pump is able to pump 26m³/day. The pump inverter/controller provides AC power to the pump and constantly supervises the system by measuring the array current, array voltage and the internal temperature. It has built-in control procedures in case of any fault detection. The PV array of the system includes 35 polycrystalline modules, 42W_p each and an average efficiency of 10%.

LESSONS LEARNED AND RECOMMENDATIONS

- One) Energy development strategies, programs, and projects directed towards meeting the needs of the poor majority are bound to fail, if no effort is made at the same time on the development of the economic, social, and technological capabilities of the rural people, as well as the infrastructure at community level.
- Two) Photovoltaic should be promoted as an energy generator to do productive work for increasing income, for effective training and for better and healthier environment.
- Three) Public participation on all phases of PV field projects, as well as appropriate training of end-users at the local level, have been stressed by all investigators and project directors to be important for the success of any project.
- Four) Small-scale PV power systems appear to have the most flexibility and reliability for meeting a large variety of small scale, decentralized, electrical energy needs of rural communities in Egypt as well as in other developing countries. There is a significant market potential for PV systems in village applications in Egypt.
- Five) It is found necessary to develop micro-organizations at the village level; a sort of rural energy cooperative to:
 - manage the new technologies introduced and sustain the on-going productive and service activities based on them,
 - integrate the different activities for a positive and comprehensive local development,
 - generate funds needed to install, operate, maintain, repair, and replace if necessary the community energy systems.
- Six) We have to pay more attention to the training and education of the local technical staff. Human resources are important for projects and programs implementation and for sustainable development.

BARRIERS AND CONSTRAINTS

With all the above advantages (see Introduction) one would have expected PV applications to spread everywhere in the world. This did not happen. Why is that? There were and still are barriers to the diffusion of this interesting technology.

Until recently, price has been the main barrier to the widespread use of PV. In 1970, for example, this was over \$100/W and in 1975 it went down to \$30/W. Since then, improvements in manufacturing technology and increased scale of production have reduced prices to their present 2000 levels of \$3/W for the modules.

The above price was not attained without improvements in other aspects of PV technologies. Improvements in conversion efficiencies, for example, had gone far from the initial 1% reported in 1940. In the late fifties, crystalline silicon cells were developed with high enough conversion efficiencies to enable their use for power generation. Development in conversion efficiencies was due to the active space program in the USA, which resulted in the launching of the first powered satellite, Vanguard I, in 1958. The output of PV modules for terrestrial applications matured around 1983 with the introduction of automated production facilities. The output then jumped 4 folds over 1991. The output kept increasing till it reached over 50 MW in 1990.

Over the past decade, the price of PV modules and systems has been steadily falling in real terms. Module prices for mono- and poly-crystalline silicon are currently around \$4/W_p for large orders exclusive of delivery cost and taxes. The use of cheaper silicon and fully automated manufacturing plants may produce further reduction of PV module prices to \$2-3/W_p. With thin film technology, further lower prices are attainable. However, crystalline silicon cells will continue to be competitive with thin film processes for several years because thin film systems are not yet suitable for power generation which is still a dominant feature of crystalline silicon systems.

An interesting research, conducted in Europe and the USA, on possible ways to incorporate social costs in decisions on energy systems concluded, taking into account the results on CO₂, that the differences of costs not included in the price of conventional energy and photovoltaic averages 10 cents/kWh for new power stations. Compared to power stations without smoke gas de-sulfurization, PV has an advantage of 12 cents/kWh. The overall range for this difference in the cost not included in the market prices of electricity runs from 4 to 19 cents/kWh. In fact comparing costs of operation and maintenance plus fuel gave the PV option a significant lead.

PV ACTIVITIES OF ELECTRONICS RESEARCH INSTITUTE

In the following we introduce the recent activities, including internal and external projects, of Photovoltaic Cells Department (Electronics Research Institute) in the fields of monocrystalline silicon solar cells preparation, thin films, and applications:

- 1986-1988 : Internal Project No. 4/2/2/1986, NRC : „Study of Photovoltaic Cells in Egyptian Circumstances and its Applications“
- 1988-1993 : Internal Project No. 4/2/6/1988, NRC : „An Efficient Combined Solar-Wind Energy System“
- 1988-1989 : Internal Project No. 7/17/1988, NRC : „Silicon and other Photovoltaic Solar Cells: Study and Applications“
- 1989 : „Technology of New Materials used in Energy and Information Field“, Academy of Scientific Research and Technology, Ministry of Scientific Research, Egypt.
- 1992-1997 : Internal Project, ERI : „New Antireflection Coating Material for Solar Cells“
- 1996-1998 : External Project, Academy of Scientific Research and Technology : „Study and Selection of the Available Technology for Mass Production of Solar Cell Modules“
- 1996-1998 : Internal Project, ERI : „Design and Implementation of an Optimum Solar Pumping System“
- 1998-2000 : External Project, Academy of Scientific Research and Technology : „Researches in the Technology of Manufacturing Electronic Components“

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3. Fuel Cells



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**Advanced SOFC Technology and its Realization at
Siemens Westinghouse**

Hermann Kabs
Siemens AG

Egyptian – German Workshop on
**Materials and Processes for Advanced Technology:
Materials for Energy Systems**

Cairo 7. – 9. April 2002

Introduction

Fuel cells are essentially simple electrochemical converters, which convert the chemical energy of the fuels directly in electric energy. They play an important role in the debate on the energy supply of the future for mainly:

- high electrical efficiency
- low emissions and
- distributed generation, that means, energy generation nearby the place of consumption.

There are several types of fuel cells in discussion for a wide range of applications and power from portable to stationary. Siemens main activities are at present in PEFC for submarines and SOFC for stationary application. By contrast with the other types of fuel cells, SOFC developers invented two basically different cell types, each still featuring several variations: a planar and a tubular cell.

After acquiring Westinghouse, Siemens decided to focus SOFC activities on the tubular design, which have been developed for many years at Westinghouse.

Design of cells, generator and systems

The single cell in the Siemens-Westinghouse (SWPC) design is partly depicted in **Fig. 1**: it is a tube with one closed end of at present 1.8 m length and 2.2 cm diameter. The supporting structure is formed by the cathode (air electrode), onto which interconnector, electrolyte and anode (fuel electrode) are deposited by different methods. It is an all-ceramic device. In general, the materials used are the conventional ones, the processes are at the moment mostly those, which are well proven in the development. On the basis of the today's technology a single cell generates somewhat more than 100 W direct current power at atmospheric pressure.

Twenty-four of these tubes are connected in parallel and series to form a bundle (see **Fig. 2**), the equivalent to a stack in a planar configuration. These bundles are electrically connected in series, 4 to form a row. They are part of the generator, that is shown in **Fig. 3**.

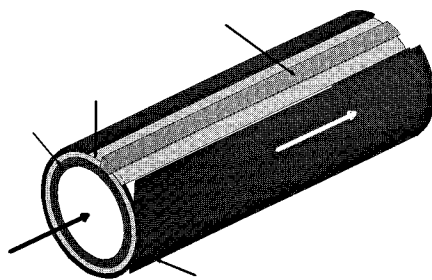


Fig. 1: SOFC tubular design of Siemens Westinghouse Power Corporation

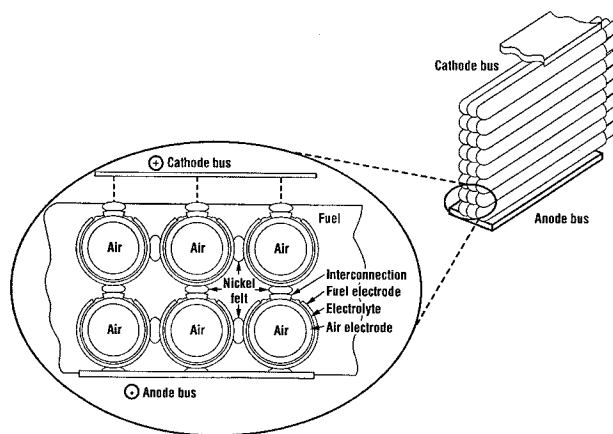


Fig. 2: Bundle configuration

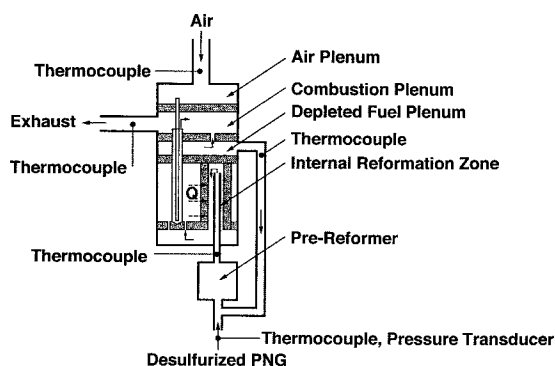


Fig. 3: SOFC generator schematic

Desulphurized natural gas flows through a prereformer in an internal reformation zone that is heated by the waste heat of the electrochemical reactor, caused by internal resistances. The hydrogen produced reacts along the tubes of the bundle by flowing from bottom to top to the depleted fuel plenum. There, the larger portion returns in a loop to the inlet, the smaller portion enters the combustion plenum, to be burned with the air after having passed the cells.

The preheated air is fed by a feeder tube to the bottom of the cells and flows to the open top in the combustion plenum.

The performance of an electrochemical cell is dependent on the partial pressure of the reactants; according to Nernst's Law. This effect is in experimental results depicted in **Fig. 4**. Based on this results, two different systems will be possible:
 one operating at atmospheric pressure for CHP application;
 one operating at higher pressure and in combination with a microturbine primarily for electricity production. The advantage of pressurized operation is a performance gain due to the increased partial pressures of the reactants.

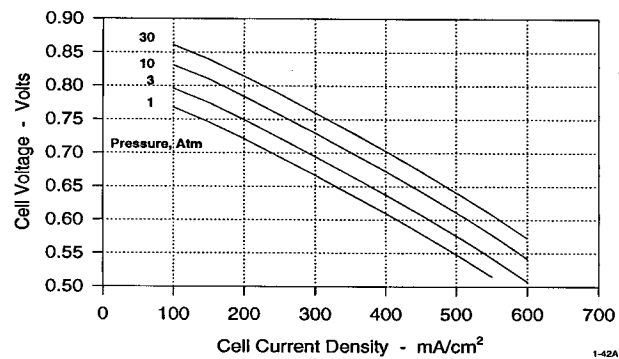
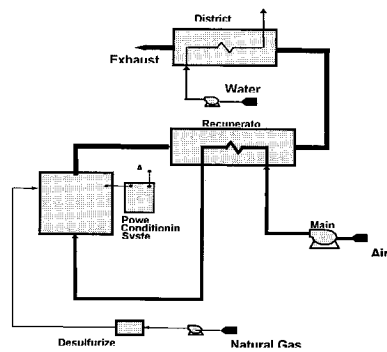


Fig. 4: Effect of pressure on SOFC voltage-current performance

The effect in practical terms is shown in **Fig. 5**, comparing calculated 1 MW systems in atmospheric and pressurized hybrid version: A lower number of cells and a higher electrical net efficiency are the most important figures.



50	Efficiency (%)	60
30	Efficiency Thermal (%)	20
80	Total Efficiency (%)	80
9216	Number Cells	5760
1.04	Pressure	3.0
Blower	Air	GT
1.0	SOFC Power (MW)	0.8
—	GT-Power (MW)	0.2

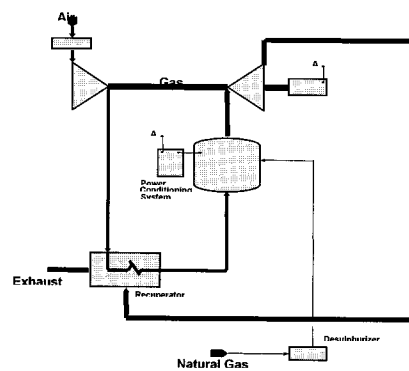


Fig. 5: Comparison of an atmospheric and pressurized system

Demonstration

A very important part in the development of any technical system is the demonstration at a customer's site in order to gain experience of complete systems in practical operation.

As **Table 1** shows, Siemens-Westinghouse started rather early in 1986 with a demonstration of a 400 W unit at TVA, and this has continued up to the present with a 220-kW unit at SCE. This list shows a continuous increase in rated power and complexity, proving the technical progress and success of the development. Besides the increase in power output, which also means an increase in cell numbers, the table indicates

- the development in cell design from a porous support tube (PST) in two steps to the cathode, forming the supporting structure (AES). It is not obvious but may be concluded that the specific power density was also increased by nearly 60% through the introduction of the AES tubes.
- the development of longer tubes
- the progress in the use of fuels, natural gas instead of hydrogen. It has to be noted that the unit SCE-2 1995 was also operated successfully with a reformat of diesel (DF-2) and jet fuel (JP-8)

Year	Customer	Stack Rating (kW _e)	Cell Type	Cell Length (mm)	Cell Number	Oper. (Hrs)	Fuel	MWh
1986	TVA	0.4	TK-PST	300	24	1760	H ₂ +CO	0.5
1987	Osaka Gas	3	TK-PST	360	144	3012	H ₂ +CO	6
1987	Osaka Gas	3	TK-PST	360	144	3683	H ₂ +CO	7
1987	Tokyo Gas	3	TK-PST	360	144	4882	H ₂ +CO	10
1992	JGU-1	20	TN-PST	500	576	817	PNG	11
1992	UTILITIES-A	20	TN-PST	500	576	2601	PNG	36
1992	UTILITIES-B1	20	TN-PST	500	576	1579	PNG	26
1993	UTILITIES-B2	20	TN-PST	500	576	7064	PNG	108
1994	SCE-1	20	TN-PST	500	576	6015	PNG	99
1995	SCE-2	27	AES	500	576	5582	PNG/DF-2/JP-8	118
1995	JGU-2	25	AES	500	576	13194	PNG	282
1998	SCE-2/NFCRC	27	AES	500	576	3394+	PNG	73+
1997	EDB/ELSAM	100	AES	1500	1152	4035+	PNG	471+
1999	EDB/ELSAM	100	AES	1500	1152	12653	PNG	1474
2000	SCE	220	AES	1500	1152	778	PNG	131

PNG = Pipeline Natural Gas, TN-PST = Thin Wall Porous Support Tube, TK-PST = Thick Wall Porous Support Tube, AES = Air Electrode Supported, PNG/DF-2/JP-8 = Logistic Fuel

Table 1: SOFC field units

In the last demonstration projects, all the lessons learned in these demonstrations have been realized and proven their reliability. An issue still open is improvement of the desulphurization, which is not simple when using internal reforming of the natural gas.

Customer requirements and Results

To gain customer acceptance and to have a chance of achieving market success, it is a precondition that the product fulfills customer requirements.

In the power generation business, these are:

- 1) High efficiency
- 2) Long-term stability

For fuel cells as electrochemical devices this is a critical issue but very important in power generation.

At present, the requirement is at least 40,000 hrs of operation with, for example, a 10 % reduction in power output, due to degradation. It is evident that this is only valid for the demonstration phase; the commercial product must exceed that.

- 3) Temperature cycling stability
- 4) Unattended operation
- 5) Part load at high efficiency
- 6) Low emissions

In the laboratory tests and demonstrations the following results were achieved with respect to these requirements:

- 1) The 100-kW demonstration unit (CHP 100) for the Dutch/Danish utility consortium (EDB/ELSAM), which was moved to RWE in Germany after the successful completion of the test, operated at 46% net electrical efficiency for nearly 20,000 hrs (see Fig. 6).

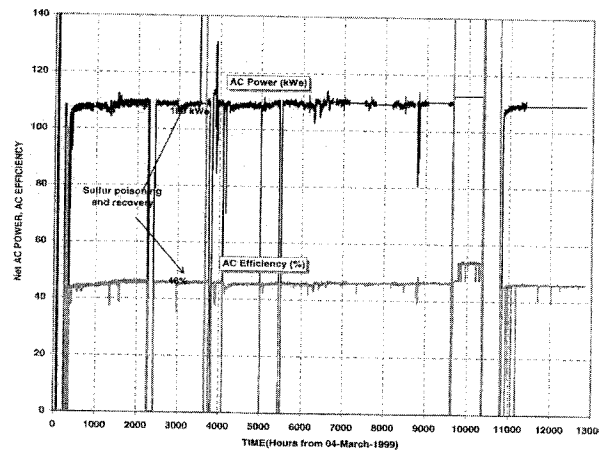


Fig. 6: Operating history 100 kW unit build 2

- 2) In laboratory tests, two SOFCs of the PST type were operated over a period of 69,000 hrs; SOFCs of the presently used AES type have operated for more than 40,000 hrs with a degradation rate of $< 0.1\%/1000$ hrs, which corresponds to 4% in 40,000 hrs. The CHP 100 operated for more than 20,000 hrs without any detectable degradation (see Fig. 7).
- 3) All systems had to undergo different numbers of steps with cooling down to ambient temperature; this caused no degradation. (see Fig. 7) "Short stacks" of four SOFCs endured more than 100 thermal cycles to ambient temperature with no effect on performance. Additionally, the unit SCE2 had been switched off in 1998 and restarted in 2000, both as standard procedures in systems operation. The restart caused no problems and the unit showed no loss in performance.
- 4) For the last systems a remote process control system was established and successfully used, which allows unattended operation.
- 5) The efficiency at part load is in the present design strongly affected by the BoP. Results with the CHP 100 unit in the Netherlands show, that within a range of 20% below rated load, the efficiency is still above 40%.

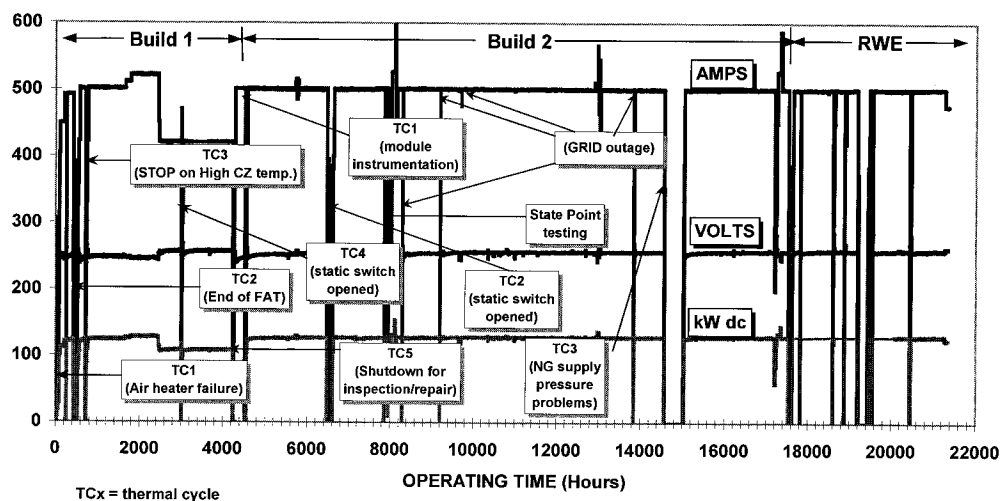


Fig. 7: Total operating history of the CHP 100

- 6) Due to the nature of the process and the requirements on fuel quality, no emissions should be expected. The electrochemical reaction runs below 1000°C, so there is no significant NO_x formation due to temperature, CO will act as a fuel and be oxidized to CO₂, S is in general an electrode poison and has therefore to be removed in a separate unit. (It has been shown, that < 10 ppm vol. and below 150 mA/cm², H₂S causes no irreversible degradation).

The exhaust gas from the CHP 100 unit contained < 0.2 ppm NO_x, no detectable CO and SO_x, also no detectable unburned hydrocarbons.

The pressurized hybrid unit at SCE, the very first of its kind, is acc. to the **Table 1** at present more than 1500 hrs. in operation. This proves the viability of the concept.

Challenges for the future

The most important issue of future activities is the reduction of cost. To tackle this key factor with a view to achieving commercial success, two main lines will be pursued:

- 1) Concentration on only a few types of machines, which are expected to meet customer requirements and to demonstrate these in sufficient numbers.
This allows improvement of system design in cooperation with customers, as well as the manufacturing processes for the fuel cell generator, which today still accounts for the largest share of the total cost.
Based on the results of a market study, Siemens Westinghouse is developing two different systems:
 - a 250-kW CHP unit operated at ambient pressure (Type CHP 250) and
 - a 500-kW pressurized hybrid unit as a combination of a pressurized SOFC generator with a microturbine generator (MTG). For the design of this system a carefully matching of the SOFC generator and the MTG is most important, modifications and development are still necessary.
- 2) Technical development for the cost reduction of the existing design and the development of a new design to increase the power density and so decrease the specific cost.
For the existing design, development of materials and processing of the components, which is suitable for mass production will be done as well as automatic assembling.
As an example for increasing the power density, the development of the so called HPD cell (see **Fig. 8**) should be mentioned.
It is expected that by using this type of cells the power density of a module will increase by a factor of 3.

In addition to these technical issues, a very important activity for future demonstrations is licensing and standardization, which will also affect system design. Even if it cannot be expected to have standards soon, this will be an important step toward commercialization.

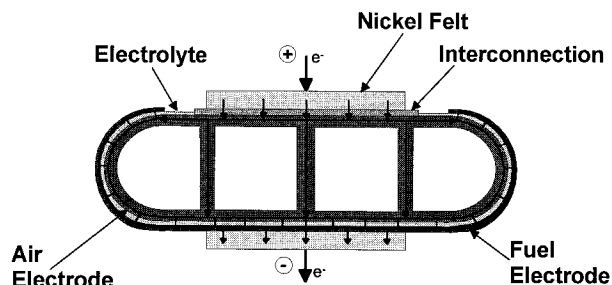


Fig. 8: High power density SOFC

Summary

The results reported indicate that the technical goals will most probably be achieved. Commercial tubular SOFC modules could be expected to have operating lives of between five and ten years. The efficiency of pressurized systems in combination with microturbines is expected to reach 57% or even higher, as an analysis shows for systems with capacities of a few MW.

The most challenging issue for the future is the reduction of cost to a level, at which the energy cost will be competitive with those of conventional systems. To meet that target, there is a well defined strategy, which should make it possible to introduce precommercial systems into the market in 2004 and commercial systems in 2007/8.

Acknowledgement

The development of tubular SOFC technology is supported by the United States Department of Energy under a cooperative development agreement; technical development is co-funded by the German Ministry of Economic Affairs. Other support is provided by our partners in the demonstration.

The support of the colleagues of SWPC SFC is highly appreciated.

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Planar SOFC Designs and Processing Methods

Hans Peter Buchkremer
Research Centre Jülich
Institute for Materials and Processes in Energy Systems
Institute 1 Materials Synthesis and Processing
52425 Jülich
Germany

1. Introduction

As direct converters of chemical to electrical energy and because of their high efficiency, fuel cells are of special significance in the energy sector. Particularly in the case of high-temperature solid oxide fuel cells (SOFCs), not only electrical energy but also heat is produced at a high temperature level (800 to 1000°C). This heat can be used in a variety of ways and plays a not inconsiderable part in determining the design of the fuel cell system, i.e. ultimately the overall efficiency of the total energy chain has to be optimized under the boundary conditions of the most economic and emission-free operating mode. In general it can be said of all fuel cells that the system design is determined by the application in question and the boundary conditions or requirements.

The basic principles of energy conversion plants with planar fuel cells will be briefly described and their special features explained. The development process is currently at such an early stage that no design nor processing method has become standard. Every variant has specific advantages and may therefore be particularly suitable for certain markets. The general opinion is that the product will find increasing acceptance in the next five to ten years and that a significance market penetration will only take place after 2010.

2. Planar Cell Design and Processing

SOFC designs are largely differentiated according to the cell geometry, i.e. tubular and planar. The tubular cell geometry is the oldest SOFC design.

Figure 1 gives an overview of important companies and institutions that have developed or still are developing planar and/or tubular SOFC concepts. In recent years, small companies have become increasingly involved in this process, which are, however, not included in this overview.

tubular		planar				
one cell per tube	several cells per tube	one cell per layer			several cells per layer	
ceramic interconnector	ceramic interconnector	metallic interconnector		ceramic interconnector	metallic interconnector	
		<u>thick electrolyte</u>	<u>thin electrolyte</u>	<u>thick electrolyte</u>	<u>thick electrolyte</u>	<u>thin electrolyte</u>
SWPC (D/USA) Toto (J)	MHI + EPDC (Nagasaki) (JP)	Sulzer (CH) ECN (NL) TMI (USA) Ztek (USA) Fuji Electric (terminated) Murata/ Osaka Gas (JP) (terminated)	FZJ (D) ECN (NL) Risoe (DK) Global Thermo-electric (CAN) Allied Signal (USA) CFCL (AUS)	SOFCo (USA) Tokyo Gas (JP) MHI+CEP (Himeji) (JP) Risoe (DK) Toho Gas (JP) Dornier (D) (terminated)	CFCL (AUS) Sanyo (JP) (terminated) Siemens (D) (terminated)	Rolls Royce (GB)

Fig. 1: Important development groups for tubular and/or planar SOFC technology

The Siemens-Westinghouse SOFC tubular concept is currently the most advanced SOFC system. Large-scale experimental facilities with a power of several 100 kW are being tested in field trials worldwide. Plants in the megawatt class, in part combined with a micro-gas turbine and operating at elevated pressure (improved efficiency), have been projected and will be installed at customers' sites (e.g. RWE, Germany) in coming years.

The second major group of SOFC systems concerns the planar arrangement of cells and interconnectors. This design is being investigated worldwide by the majority of companies and research institutions involved and developed to commercial maturity. Interest in this design is based on the following potential advantages:

- higher power densities can be achieved
- simpler integration of metallic components
- reduction in operating temperature seems to be easier by employing metallic structures.

Figure 2 shows the schematic layout of a conventional planar cell. The support structure here is the 150- to 200 - μ m-thick electrolyte (gastight), which is coated on both sides by porous electrodes about 50 μ m in thickness. The interconnector required to connect the

single cells can be either of metallic or ceramic design. It frequently also undertakes the function of gas supply and is therefore equipped with gas ducts (Fig. 3).

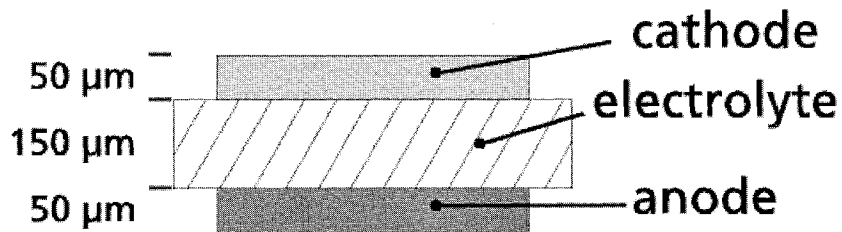
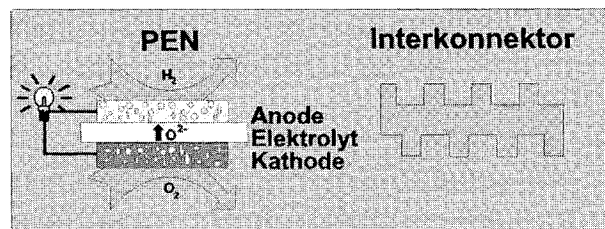


Fig. 2: Basic scheme of a conventional planar SOFC



Anode:	Reaktion: $\text{O}^{2-} + \text{H}_2 \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ elektronenleitend porös Reaktionskatalysator
Elektrolyt:	Sauerstoffionenleiter Leerstellenleiter keine Elektronenleitung gasdicht
Kathode:	Reaktion: $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$ elektronenleitend porös Reaktionskatalysator
Interkonnektor:	Elektrische Verbindung der PENs elektronenleitend gasdicht

Fig. 3: Planar SOFC cell and interconnector (schematic) and the function of the individual components

There are a wide variety of detailed variants of the planar design (examples are given in Figures 4 – 7).

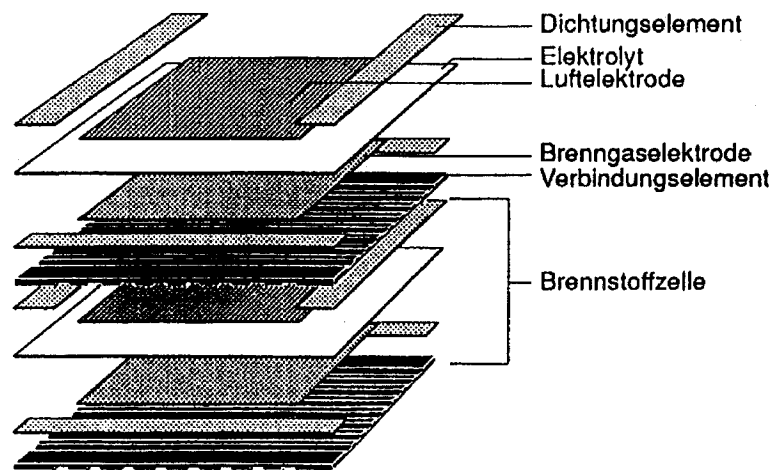


Fig. 4: All-ceramic design and interconnector with cross-flow design (Daimler-Dornier system)

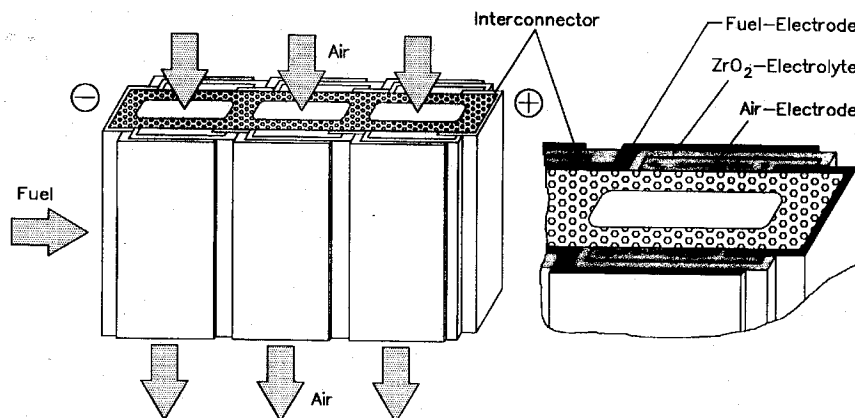
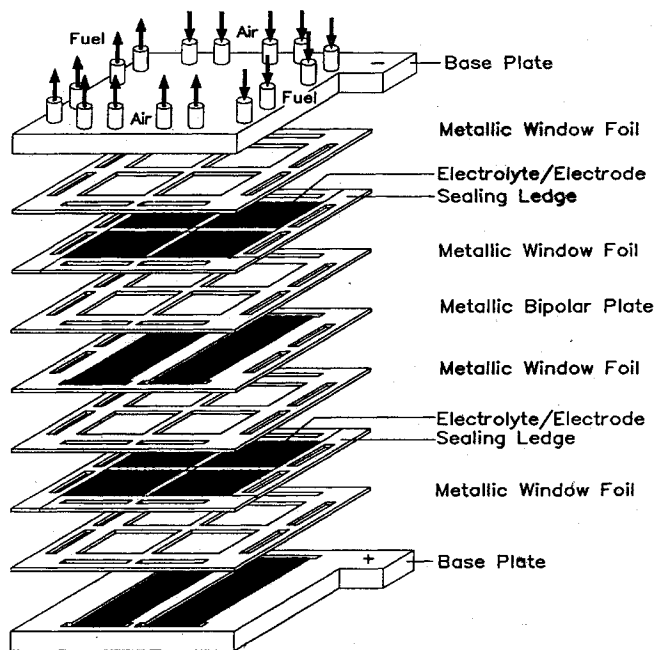


Fig. 5: All-ceramic design of a planar cell arrangement (ABB design)

The conventional electrolyte-protected SOFC cannot be scaled up as required due to the relatively thin electrolytes (mechanical strength). To date, no cells larger than approx. 150 x 150 m² are manageable in a stack. So-called "window designs" were developed in order to increase the cell area, so to speak. In this case, not just one cell is present per stack level but several. The individual cells are fixed in a frame and the interconnector is designed accordingly. Such a system makes high demands on the contact zone and sealing of the individual levels.



Source: CEC 1991

Fig. 6: Window design for planar SOFC with metallic interconnector (Siemens design)

A general problem of all planar systems is sealing off the gas compartments of the anode and cathode and also sealing them off from the environment since the seal must remain functional at high operating temperatures and also in the unavoidable temperature cycles. Most system designs use glasses or glass ceramics for sealing purposes, i.e. completely or partially crystallized glasses. Proper functioning of this arrangement requires exact matching of all the relevant thermal expansion coefficients of the cell and stack components to each other because otherwise the sealing points would be destroyed by the mechanical loads occurring during thermocycling.

Planar cylindrical cells with a metallic interconnector, integrated heat exchanger and afterburner for the unused fuel gas have been developed by Sulzer-Hexis for the power/heat supply of domestic and commercial users. Plants with power ratings in the kW range are practically ready for mass production and are being tested in field trials (Fig. 7, Tab. 1)

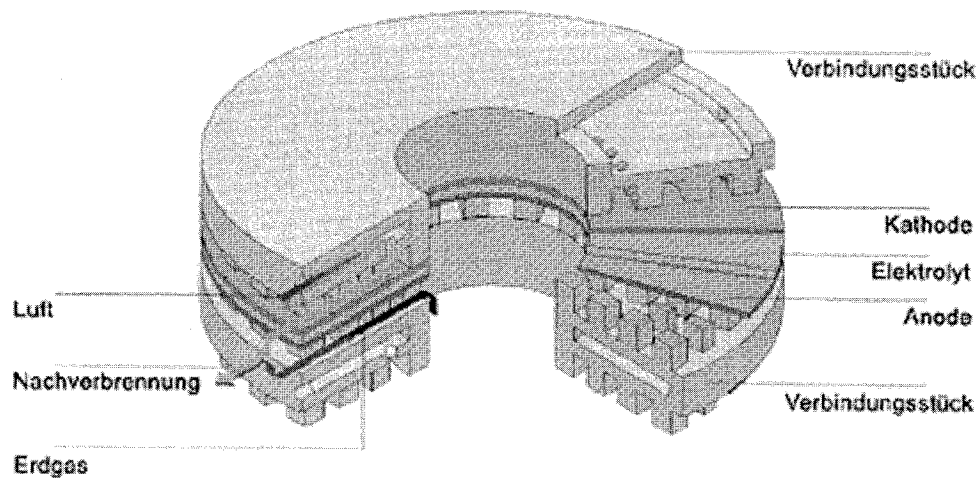


Fig. 7: Cylindrical planar cell design with metallic interconnector from Sulzer-Hexis

Tab. 1: Technical data of a 70-cell stack (Sulzer-Hexis)

diameter	120 mm
height	518 mm
number of cells	70
total cell area	0.7 m ²
operating temperature	950 °C
stack voltage	39 V
stack current	27 A
electric power	1053 W
fuel gas	natural gas (low pressure grid)

2.1 Electrode- and electrolyte-supported designs

In addition to the distinguishing feature of planar or tubular, the mechanical support component in the cell is of decisive significance for the operating performance and the achievable performance data of the system. It is immediately obvious that the feasible cell size is a function of the strength of the support structure. For this reason, this support function would be assigned to the high-density electrolyte if there were not other reasons for not doing so. Due to the electrical resistance of the electrolyte (zinc oxide), a supporting electrolyte is restricted to a minimum operating temperature of approx. 850 – 900 °C. As already mentioned, efforts are being made to reduce the operating temperature to less than 800 °C. However, such low temperatures require thin electrolyte layers which cannot tolerate such high mechanical loads. These considerations led to the development

of electrode-supported designs for both planar and tubular systems. In the all-ceramic designs, the aim was to increase the power density because it was not possible to reduce the temperature due to the poor conductivity of the ceramic interconnector. Designs using metallic interconnectors are able to exploit the full potential of any possible temperature reduction. Electrode-supported designs operate with thin electrolyte layers in the range of 5 μm to 40 μm . Cost, fabrication and design aspects decide whether the cathode or anode is used as the support structure. A typical representative of a cathode-supported design is the Siemens-Westinghouse system.

Figure 8 shows the anode-supported SOFC concept developed by Research Centre Jülich (substrate concept, the anode is often termed the substrate here) with the materials used and the specifications. Mechanically speaking, each single cell is supported by the anode substrate (1 – 1.5 mm thick). Due to the high mechanical stability of the substrate, the cell area can be significantly larger than in the electrolyte-supported design. The electrolyte is now only about 5 – 10 μm thick, which enables the operating temperature to be reduced to about 750 $^{\circ}\text{C}$ thus leading to a considerable reduction in system costs with at the same time a high power density.

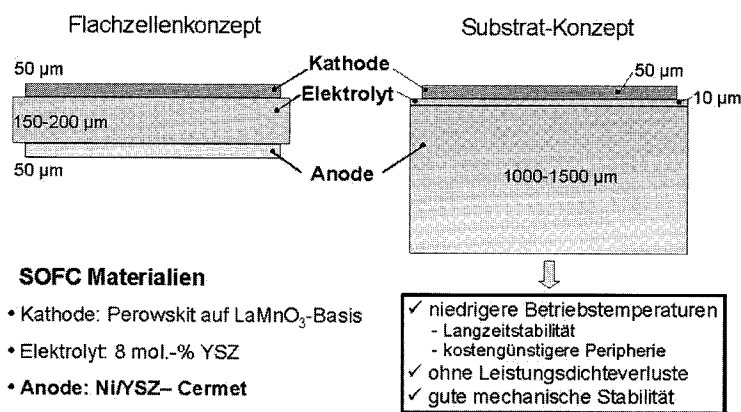


Fig. 8: Basic structure of an anode-supported SOFC with thin electrolyte (right) in comparison to a conventional electrolyte-supported design (left)

Figure 9 shows the materials used for an anode-supported concept and the schematic arrangement of the major stack components. Depending on the design of the metallic interconnectors (Fig. 11), both parallel- and also cross-flow gas supply (Fig. 10) can be used.

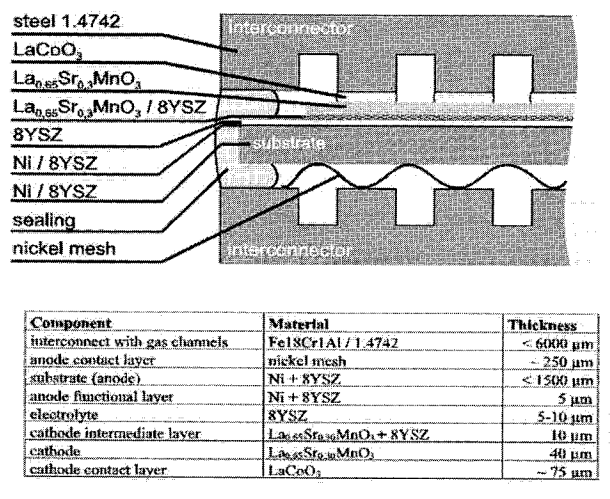


Fig. 9: Schematic layout of an anode-supported SOFC concept (Research Centre Jülich (FZJ) concept)

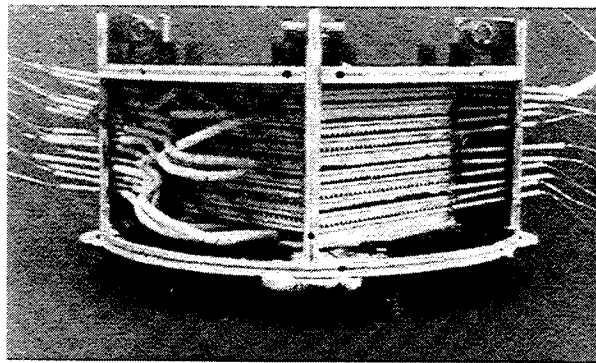


Fig. 10: Open experimental stack – 10 cells 10 x 10 cm² stack open and equipped with thermocouples (FZJ concept, c-design)

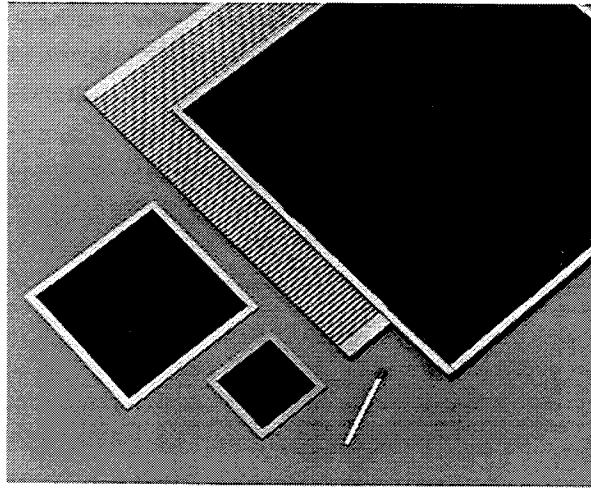


Fig. 11: Single cells of various sizes and metallic interconnector with gas ducts (c-design)

2.2 Metallic and ceramic interconnector

Both types of interconnector are used mainly in planar arrangements.

The advantages of metallic interconnectors are:

- low cost
- variety of designs
- not brittle
- large geometries feasible
- high electrical conductivity
- suitable for low operating temperatures.

Aspects speaking in favour of ceramic interconnector arrangements are mainly chemical resistance at operating temperature and great stability. The chemical stability means that practically no chromium compounds evaporate during operation reducing the electrochemical effectiveness of the cathode in long-term operation, which becomes apparent in an increased ageing of the stack. Furthermore, the contact resistances of the metallic interconnectors are increased at the interface to the cathode due to oxide formation. This oxide formation can lead to failure of the stack during thermal cycling due to spalling.

Important development goals for metallic interconnectors are therefore:

- slow growth of oxide layers on the surface
- avoidance of insulating surface layers (e.g. no Al_2O_3 formers)
- thermal expansion behaviour adapted to the cells
- avoidance of chromium evaporation.

These requirements can currently only be realized by the additional application of thin functional layers. By way of summary, it can be said that metallic interconnectors have the potential for stable, long-term stack operation at low temperatures. However, this still has to be demonstrated in practical application. This proof has already been demonstrated for ceramic interconnectors, but the latter are not suitable for temperatures significantly below 900 °C (electronic conductivity).

2.3 External and internal gas distribution

The type of gas distribution (manifolding) to supply the cell plays a decisive role in the choice of design. One speaks of external gas distribution in a stack if the cells are supplied externally from a gas diffusor. Gas collection is performed in a corresponding manner (Fig. 12, 13).

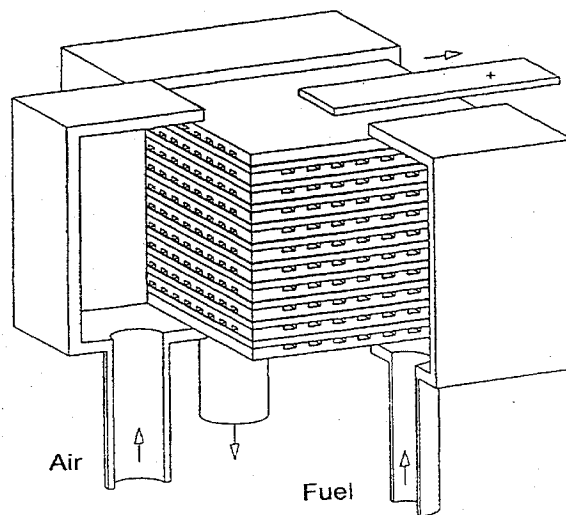


Fig. 12: 10-cell SOFC stack with external manifolding and cross flow (schematic diagram)

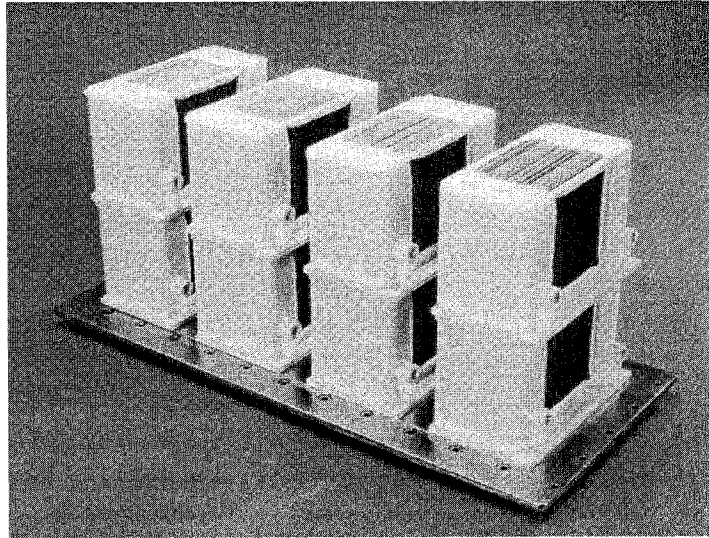


Fig. 13: Modular design (8 stacks of 40 cells each, all-ceramic, 2 kW) with external manifolding and cross flow (source: Dornier)

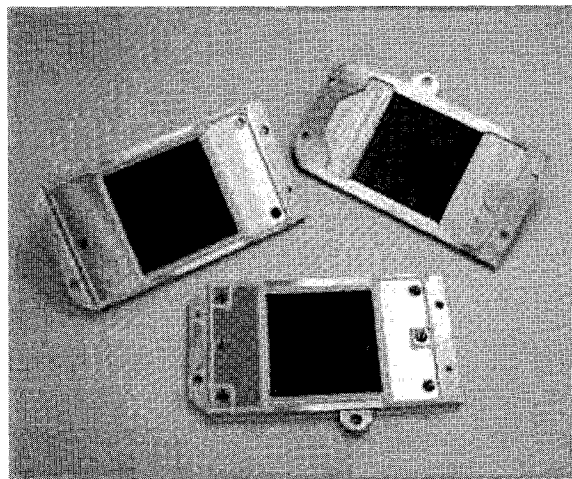


Fig. 14: Interconnectors for an anode-supported SOFC stack with internal gas distribution for 10 x 10 cm² cells and parallel flow arrangement (FZJ design)

In the case of internal manifolding, the fuel is distributed and collected inside the stack (Fig. 6, 14).

SOFC designs may be greatly dependent on the respective application. Typical distinctions are found, for example, between stationary and mobile applications. The power-heat regime required is a decisive parameter in plant design. In SOFC stacks, a basic distinction is made between tubular and planar concepts, the tubular system being the most advanced with plants in the MW class already having been designed. Planar SOFC systems in the kW class are being tested in field trials for domestic supply. The choice of thickness of the electrolyte layer and thus also the mechanical support components determines the lower operating temperature and the feasible power density. The highest power densities and low operating temperatures (750 °C) can be achieved today with planar designs. The planar design with thin electrolytes has a particularly high development potential. The question of the use of metallic or ceramic interconnectors is closely linked to the desired working temperature and the ageing rate of the SOFC fuel cell stack. Whereas ceramic interconnectors are more chemically inert, greater efforts are needed for surface protection with metallic interconnectors. However, the high conductivity of metals makes them especially attractive for low-temperature applications (600 to 750 °C) also from the cost perspective. The geometrical complexity of the interconnector and the cells is frequently decisive for the choice of internal or external manifolding. Internal manifolding opens up the possibility of parallel gas supply in the stack, which is usually desirable for reasons of temperature distribution. Since the components are geometrically easier to design external manifolding is often a space- and cost-saving solution.

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INTERCONNECTOR MATERIAL FOR SOLID OXIDE FUEL CELLS (SOFC)

K. EL Menshawy¹ , H.P. Buchkremer² , D. Stoever²

**1. Atomic Energy Authority, Cairo, Egypt
2. IWV-1, Research Centre Juelich, Juelich, Germany**

Abstract

Among the various solid oxide fuel cell (SOFC) designs now under consideration, planar concepts are favoured for large scale systems. In this configuration the ceramic electroactive cell elements consisting of anode, electrolyte and cathode are arranged between the interconnector plates. In this design the interconnector plates act as an electrical connection between the various cells, a mechanical support for the ceramic plates, provide the gas-proof separation of the gaseous fuel and oxidant and distribute them in counter flow directions. These functions together with the operating temperature of the fuel cell play a key role in the selection of interconnector material. Formation of Cr_2O_3 scale and mixed spinel oxide after long-term operation of the SOFC is of prime concern regarding performance degradation. Developers of planar configuration SOFC system have suggested and evaluated some stainless steel alloys which may satisfy the requirements of the metallic interconnector. Some trends are considered to improve the performance of these alloys and efforts are made to obtain improved knowledge and better understanding of the connector properties after long-term operation of the SOFC. This presentation deals with the function and requirements of the metallic interconnector as well as the developed alloys and possible modifications.

Introduction

In the planar configuration solid oxide fuel cell the electroactive cell elements are arranged between two interconnector plates. So the interconnector plates in this design act as;

- electrical connection between the various cells.
- mechanical support for the ceramic plates.
- gas proof separation between fuel (H_2 or natural gas) and oxidant (O_2 or air), and distribute them in counter flow directions.

Under operating conditions, the interconnector material is subjected to;

- high operating temperatures (800 – 950 °C).
- oxidizing (cathode side) and reducing (anode side) environments.
- thermal stresses.

Material Requirements

Taking into consideration the above mentioned functions and operating conditions, the interconnector material should have;

- microstructural and mechanical stability at the operating temperatures
- chemical compatibility with the contacting cell elements.
- high electrical conductivity.

- resistance against oxidizing and reducing environments.
- thermal expansion characteristics comparable to those of the other cell components.

Evolution of Interconnector Materials

These requirements can be easily fulfilled to a great extent by a number of ceramic materials than by commercially available metals and alloys. LaCrO_3 – based ceramics doped with Sr, Ca or Mg may be chosen as interconnector material for high temperature SOFCs ($\approx 1000^\circ\text{C}$) because of their sufficient electrical conductivity and high temperature stability [1]. This ceramic interconnector is mainly used with the all ceramic high temperature SOFC and is difficult to fabricate by conventional routes. The use of metallic interconnector rather than the LaCrO_3 – based ceramic material offers the following advantages

- high electrical conductivity
- high ductility
- better workability
- high heat conductivity

From the view point of oxidation resistance both Al_2O_3 and Cr_2O_3 – forming alloys are candidate materials for SOFC interconnector applications [2]. However, Cr_2O_3 – forming materials are more suitable since the Al_2O_3 layer formed at the operating temperatures of the SOFC ($\approx 950^\circ\text{C}$) is an insulating material. Commercially available Cr_2O_3 – forming alloys (Fe -, Ni -, and Co – base) are suitable for this purpose, but their main drawback is their much higher thermal expansion coefficient compared to those of the other cell components.

It is important to mention here that pure Cr has suitable thermal expansion coefficient but it has poor mechanical properties (poor ductility and toughness) which limit its application as structural material. Some Cr_2O_3 - forming ODS alloys have been developed which have better mechanical properties than pure Cr; (Cr – 5 Fe – 1 Y_2O_3 , Ni – 20 Cr- 0.5 Y_2O_3 , Fe – 20 Cr-4.5Al /1 Y_2O_3). Much attention has been paid to the alloy Cr – 5Fe – 1 Y_2O_3 . This alloy showed;

- high temperature tensile properties
- high temperature creep strength
- low thermal expansion coefficient

One of the main factors which should be considered in using Cr_2O_3 – forming alloys for SOFC interconnector applications is the evaporation of volatile Cr– bearing species [2] specially at the cathode side. In dry air CrO_3 is formed, while in wet air Cr-Oxihydroxide [$\text{CrO}_2(\text{OH})_2$] is formed. These volatile Cr– bearing species can deteriorate the function of the SOFC in two ways;

- (One) during operation of the SOFC these species can be reduced to solid Cr_2O_3 and this leads to inhibition of the O_2 reduction reaction required for cell operation.
- (Two) the volatile species react with LaMnO_3 – base cathode forming spinel oxide of the form MnCr_2O_4

To reduce the evaporation process LaCrO_3 – based coating layer can be applied over the interconnector surface (the partial pressure of Cr- bearing species over LaCrO_3 – based coating is much lower than over Cr_2O_3 scale).

Current Status of the Interconnector Material

Efforts are being made to decrease the operating temperature of the SOFC (from around 1000°C to about 800°C) and at the same time keeping the power density and

durability at the same level as at high operating temperature. Of course, the lower the operating temperature, the less severe are the requirements of oxidation resistance.

Commercially available high Cr ferritic steels do not possess the required physical, mechanical and chemical properties required for the interconnector material [3]. To fulfil these requirements, the steel composition should be carefully selected;

- the Cr content should be above 22% [4] with some minor additions of Mn, Si or Al
- decreased growth rate of Cr_2O_3 scale and good adherence can be obtained by minor additions of REE (La, Y, Hf).
- enhanced electrical conductivity of the Cr_2O_3 scale formed can be achieved by suitable minor additions of alloying elements which lead to doping of chromia. In this regard, some information are available [5] in the range of SOFC operating conditions (800 – 1000 °C and at near atmospheric oxygen pressure) ;
- (One) the presence of 0.5 wt % Y_2O_3 or La_2O_3 in Cr_2O_3 increased the electrical conductivity about 5 – 10 times (Fig.1,2)
- (Two) the presence of NiO (up to 1%) significantly increased the electrical conductivity of Cr_2O_3 , (about 2 orders of magnitude) (Fig.3)
- addition of elements that keep the thermal expansion coefficient very near to that of the other cell components; Mo, W and Co decrease the thermal expansion coefficient of α - Fe [6-8]. In the case of Fe – Cr ferritic steels Mo and W have the same effect but there is no available data on the effect of Co

A series of Fe–Cr based ferritic alloys have been developed taking into consideration the basic requirements of the interconnector material. These alloys are now being evaluated. Some results are available;

- X – ray diffraction patterns showed formation of Cr_2O_3 and (Mn, Cr) $_3\text{O}_4$ spinel oxide both under oxidizing and reducing environments after 1000 hr operation at 800 °C. Of course, the amounts of oxides are higher under oxidizing conditions.
- oxides of minor alloying element additions were also detected.

A working programme has been initiated by the authors to obtain improved knowledge and to have better understanding of the possible changes in the electrical conductivity of Cr_2O_3 and the spinel oxide formed on these alloys as a result of the presence of some possible dopants arising from the contact with other cell components or from the steel itself. In the framework of this programme Cr_2O_3 samples containing 2 and 5 mole % TiO_2 and CuO were prepared. Also, different manganese oxides; (Mn_2O_3 , Mn_3O_4 and MnO) were added to chromia in certain amounts to realize nearly the same chromium atomic fraction (about 65.4) in the mixed oxide with different Mn–valency. The electrical conductivity of Cr_2O_3 containing TiO_2 , CuO, or different Mn–oxides was measured in oxidizing and reducing atmospheres (simulating the operating conditions of the SOFC at the cathode and anode sides) in the 500 – 900 °C temperature range.

Preliminary results indicate that under oxidizing conditions (Fig. 4a) and above 750°C the presence of 5 mol % TiO_2 in chromia increased its electrical conductivity while addition of 2 mol % TiO_2 does not lead to significant changes. Below this temperature limit both TiO_2 additions decreased the electrical conductivity. Under reducing conditions the conductivity level of Cr_2O_3 is considerably shifted towards higher values (Fig. 4b), however, addition of 5 mol % TiO_2 showed a positive effect over the investigated temperature range. Chromia doped with 2 mol % TiO_2 exhibited much lower conductivity values.

Additions of CuO increased the electrical conductivity of Cr_2O_3 under oxidizing conditions. Figure 5 a shows that $\text{Cr}_2\text{O}_3 - 2 \text{ mol } \% \text{ CuO}$ has 5 – fold greater conductivity values compared to pure Cr_2O_3 . The effect is smaller for $\text{Cr}_2\text{O}_3 - 5 \text{ mol } \% \text{ CuO}$. In the reducing atmosphere (Fig. 5b) the conductivity of Cr_2O_3 is shifted to higher values while that of $\text{Cr}_2\text{O}_3 - \text{CuO}$ system remained practically around its values under oxidizing conditions giving rise to negative effect of CuO.

Different manganese oxides added to chromia decreased its electrical conductivity in oxidizing atmosphere (Fig. 6a). The magnitude of this decrease was nearly the same for the different Mn–oxides and becomes more significant as the temperature is decreased. The electrical conductivity of pure Cr_2O_3 and $\text{Cr}_2\text{O}_3 - \text{Mn}_2\text{O}_3$ system is shifted to higher values under reducing conditions (Fig. 6b), however, lower conductivity values were observed for $\text{Cr}_2\text{O}_3 - \text{Mn}_2\text{O}_3$ compared to pure Cr_2O_3 . The conductivity values of $\text{Cr}_2\text{O}_3 - \text{Mn}_3\text{O}_4$ and $\text{Cr}_2\text{O}_3 - \text{MnO}$ systems remained nearly at the same level as in oxidizing atmosphere. This implies negative effect of Mn_3O_4 and MnO in the reducing atmosphere. More work is needed for acceptable interpretation of these results. Also, the behavior of ternary systems based on Cr_2O_3 must be investigated .

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MATERIALS FOR SOLID OXIDE FUEL CELLS

By

MAGDI M NASRALLAH
*Professor of Materials Engineering
Department of Metallurgy
Faculty of Engineering
Cairo University*

Presented at

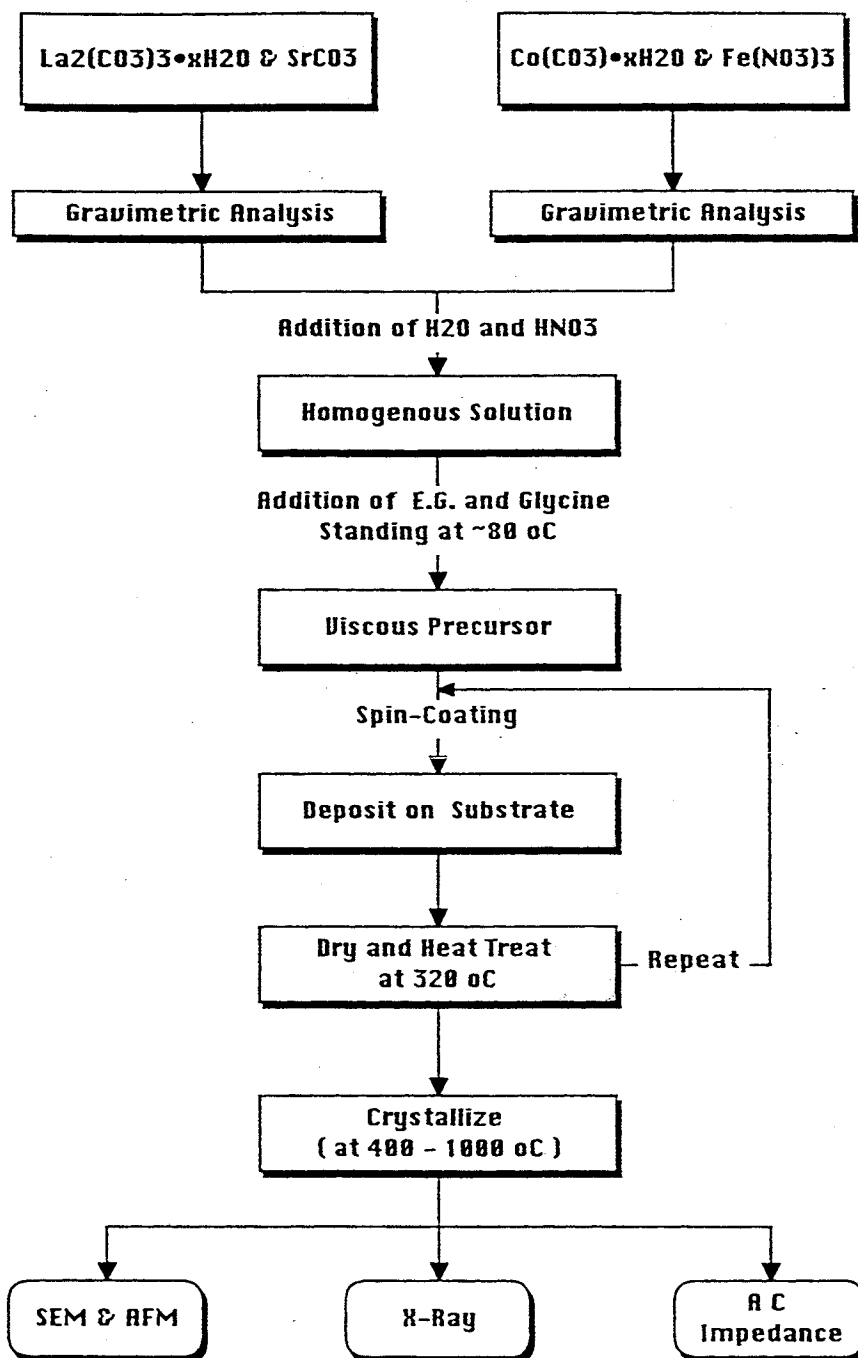
The “Egyptian-German Workshop”

On

Materials and Processes for Advanced Technology

April 2002

Experimental Procedure



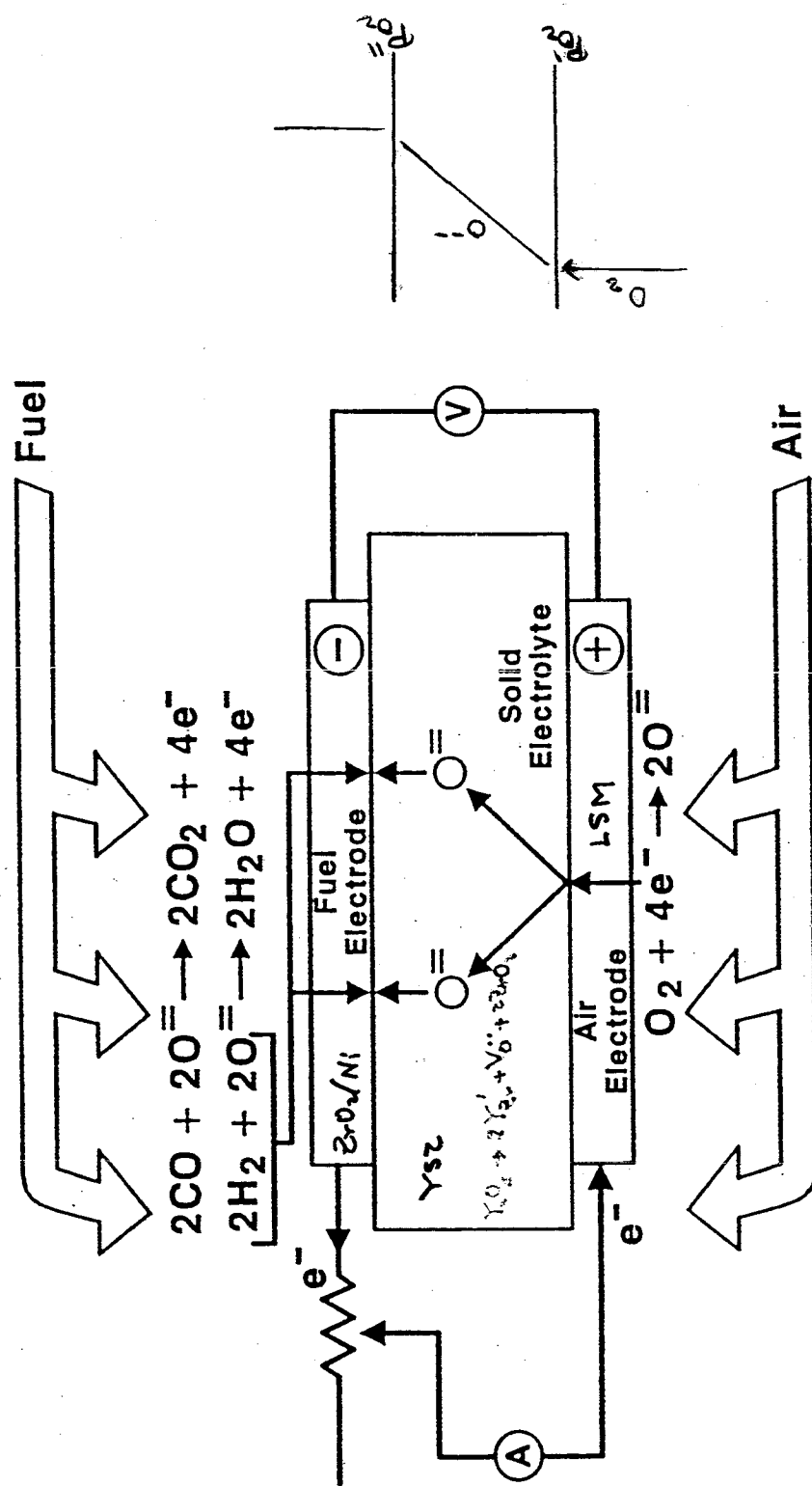


Figure 3 - Operating principle of a solid oxide fuel cell.

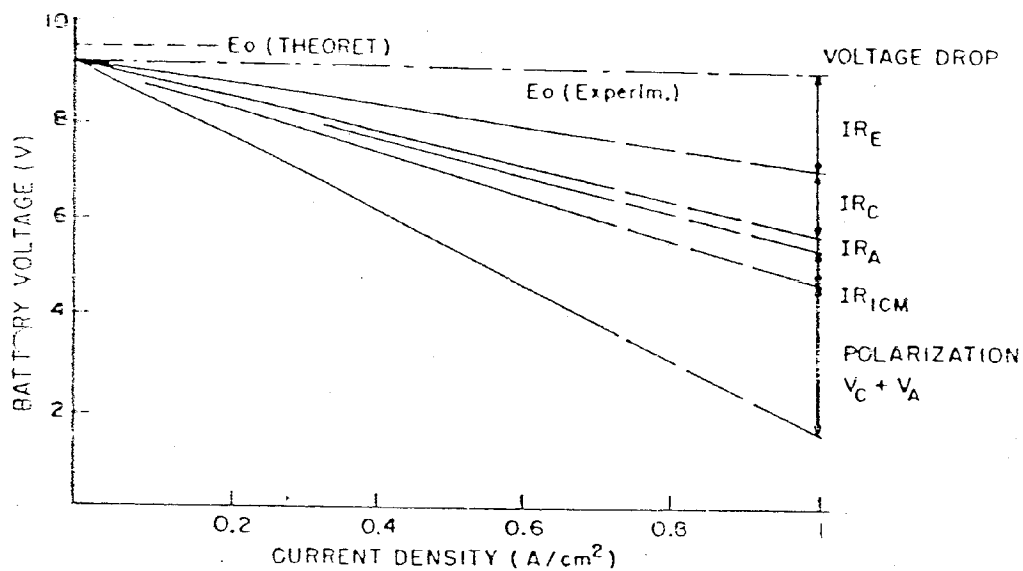
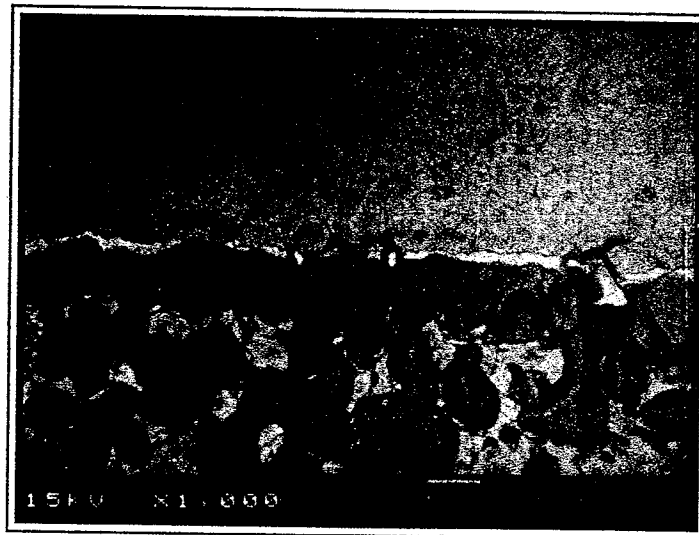


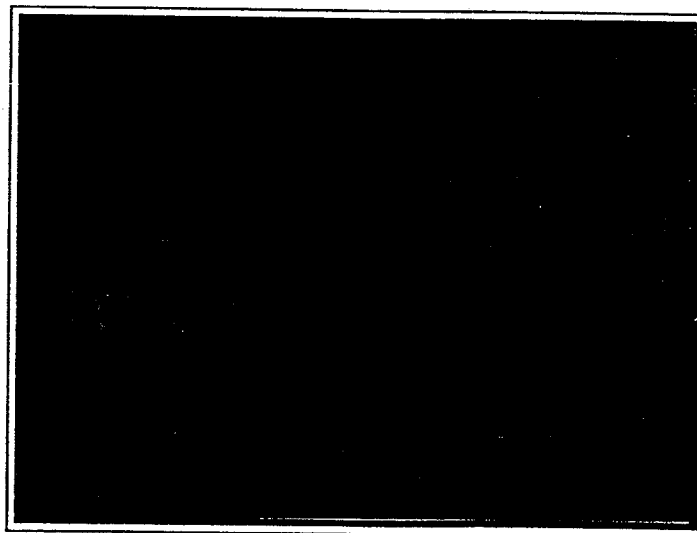
Figure 6 Resistance Polarization and Voltage Losses of a 10-cell Stack at 1000°C. Electrolyte $ZrO_2Y_2O_3-Yt_2O_3$, thickness ≥ 0.4 mm (Ref. 12). Air/Fuel H_2 (H_2O Saturated at 70°C).

Major losses

Electrolyte resistance	26%
Cathode "	16
Cathode & Anode Polarization	39
	81



(a)



(b)

SEM micrographs of LSM/YSZ interface after firing at 1300°C for
(a) 100 hrs (b) 400 hrs.

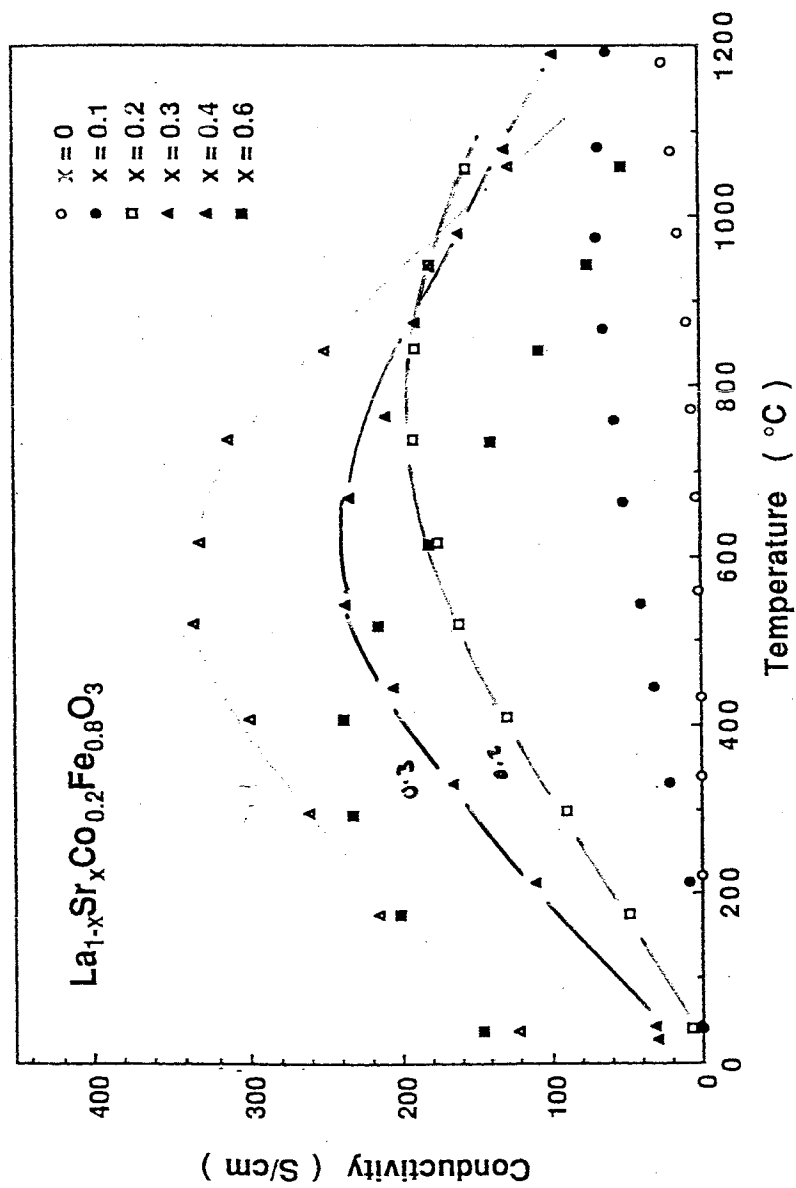
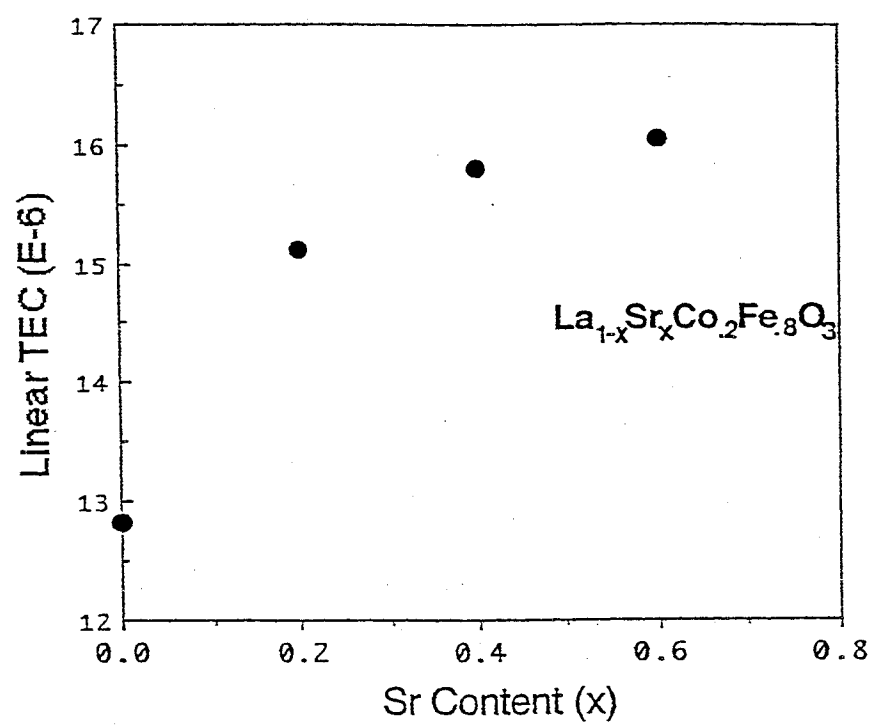
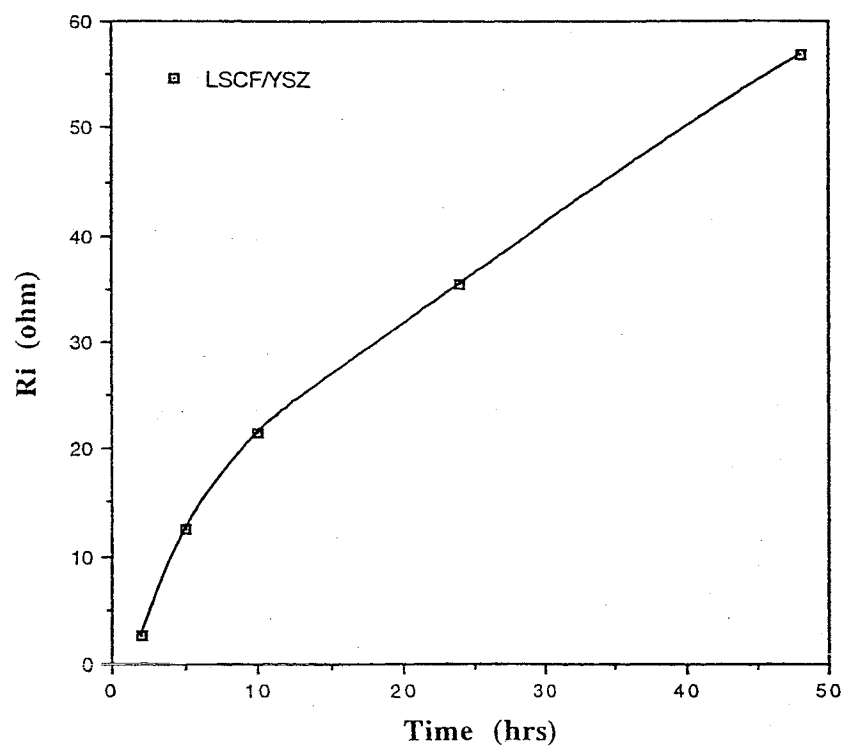
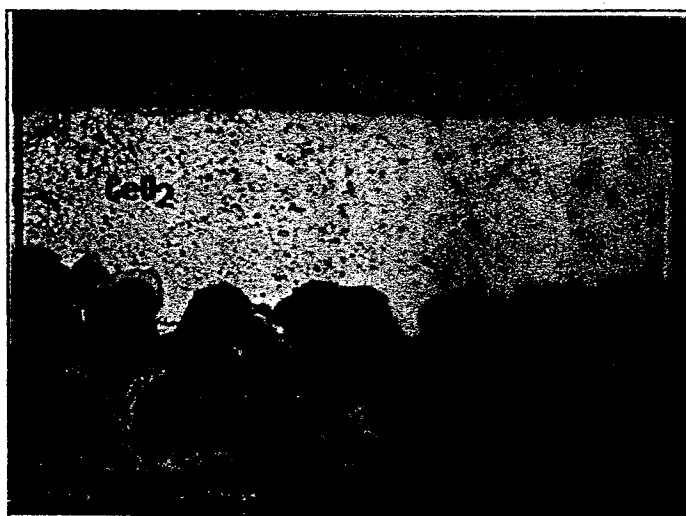


Fig. Electrical conductivity of selected LSCF as a function of temperature, in air.





Time dependence of interface resistance of LSCF/YSZ at 800°C



SEM micrograph of LSM/CeO₂/YSZ (1300°C, 400 hrs)

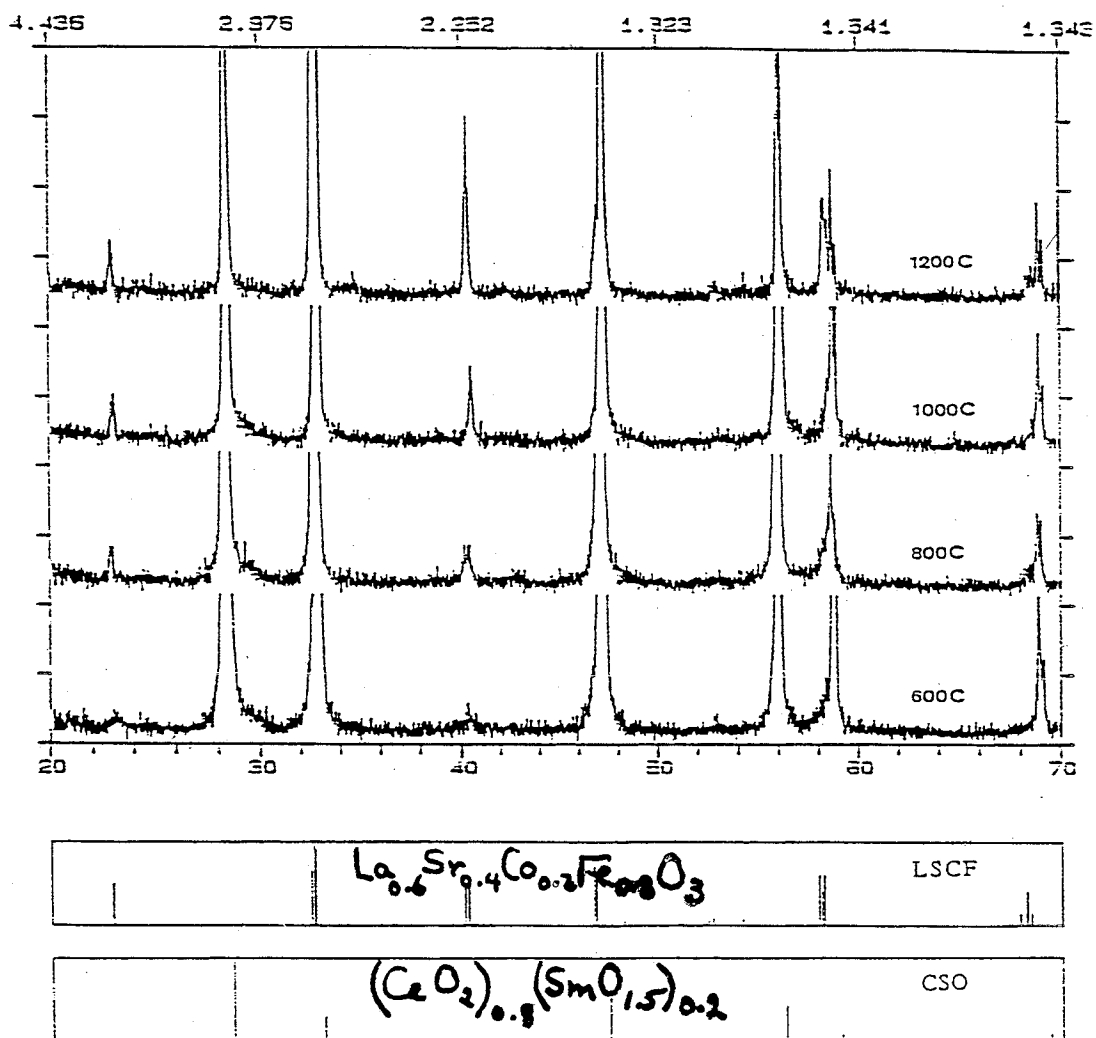


Fig. XRD patterns of the as-deposited LSCF film on CSO substrate after annealing between 600°C and 1200°C for 2 hrs.

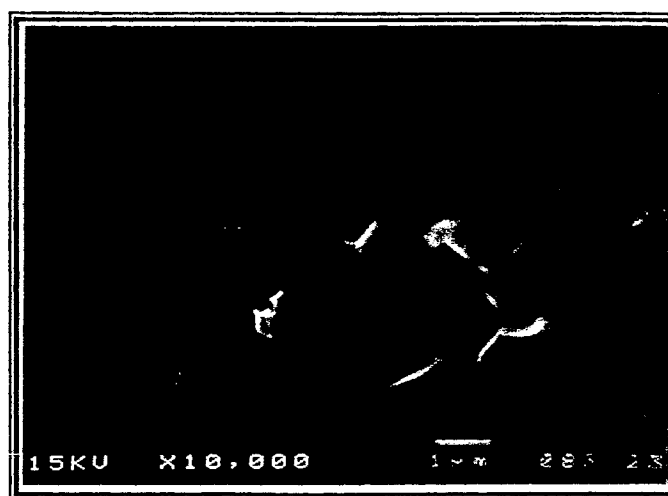


Fig. 6 Cross-section SEM micrograph of the CSO film on LSCF substrate after five spin-coatings and fast firing at 600°C for 1 min.

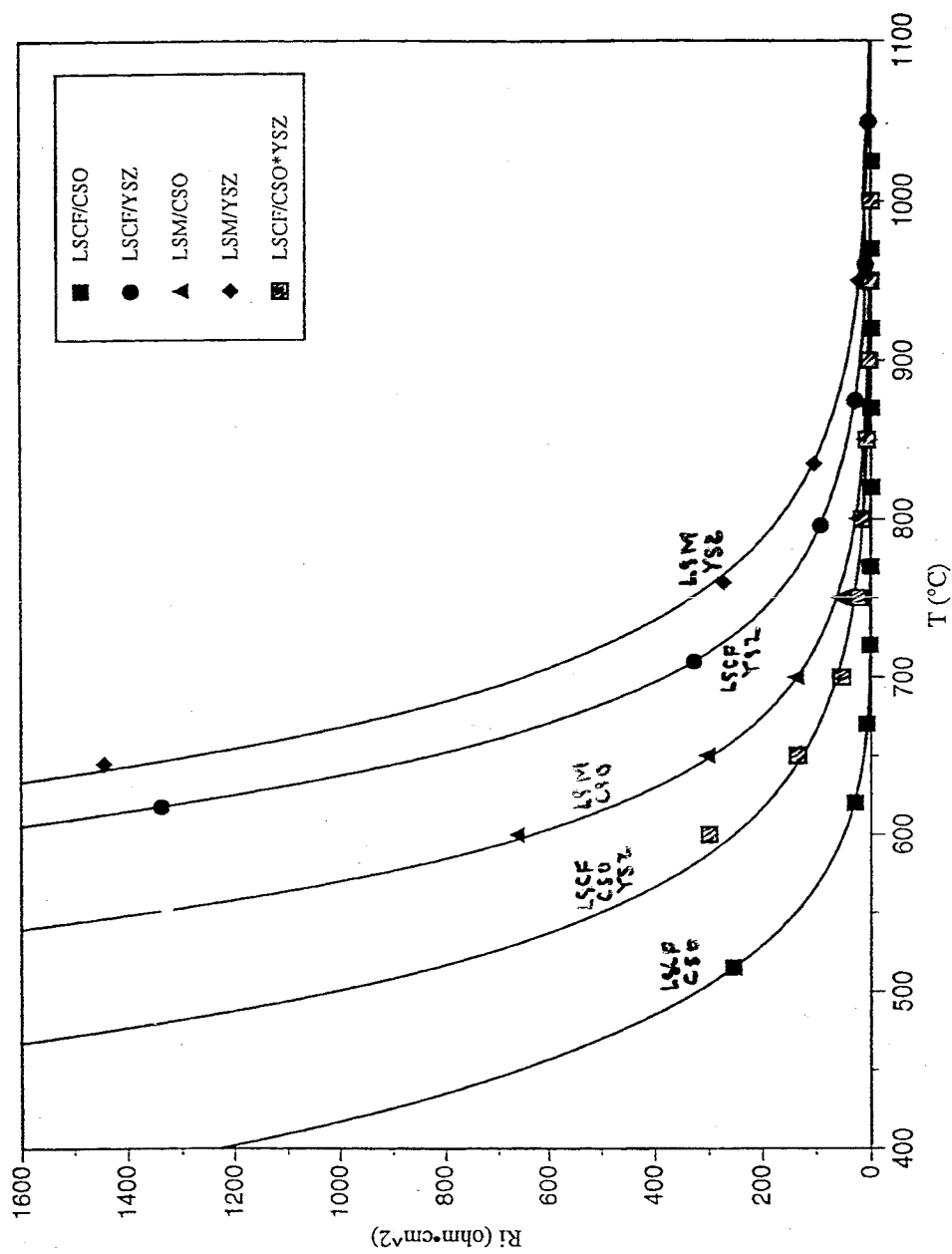
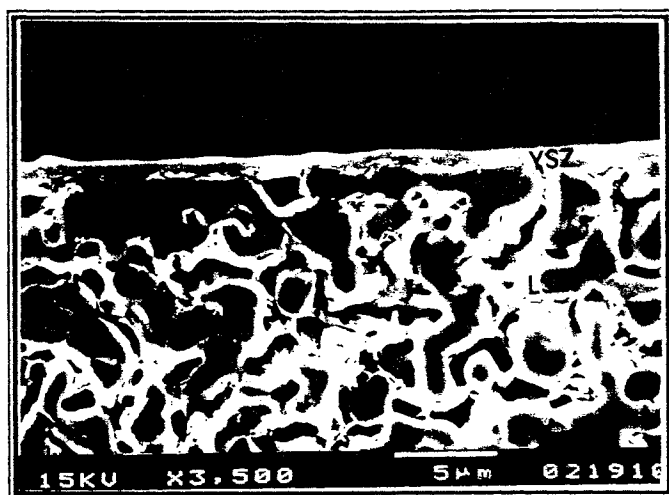
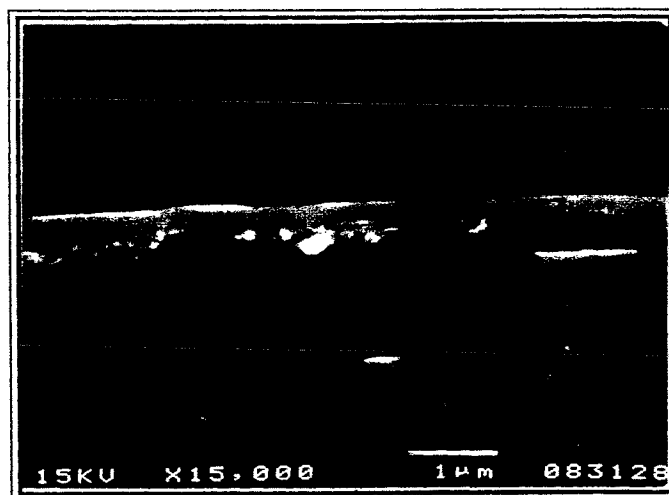


Fig. 9 Plots of interface resistance/cm² (Ri) versus temperature for various systems.



(a)

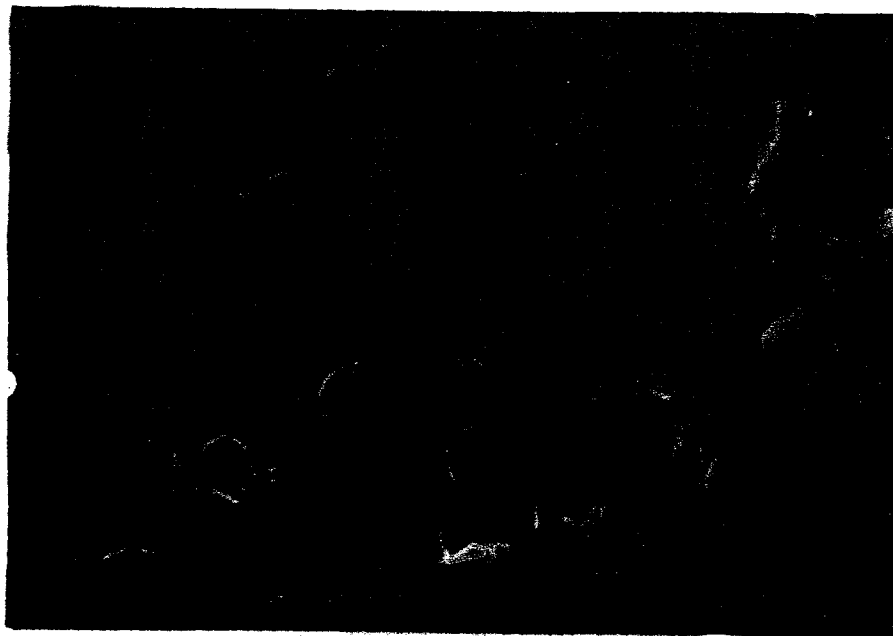


(b)

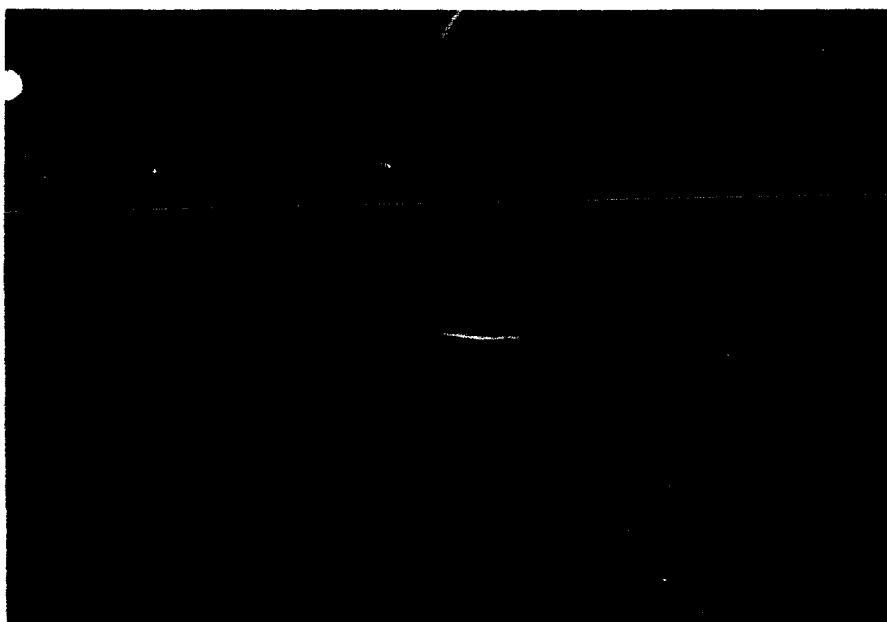
INTERCONNECT

CHALLENGES

- *Stability within Entire P_{O_2} Range*
- *Dense Micro Crack Free*
- *No Interactions*
- *High Conductivity*
- *Matching TEC*
- *Sinterable in Air at Temp. not Exceeding 1200°C*



La_{0.8}Ca_{0.2}Cr_{0.8}Li
1200°C for 1

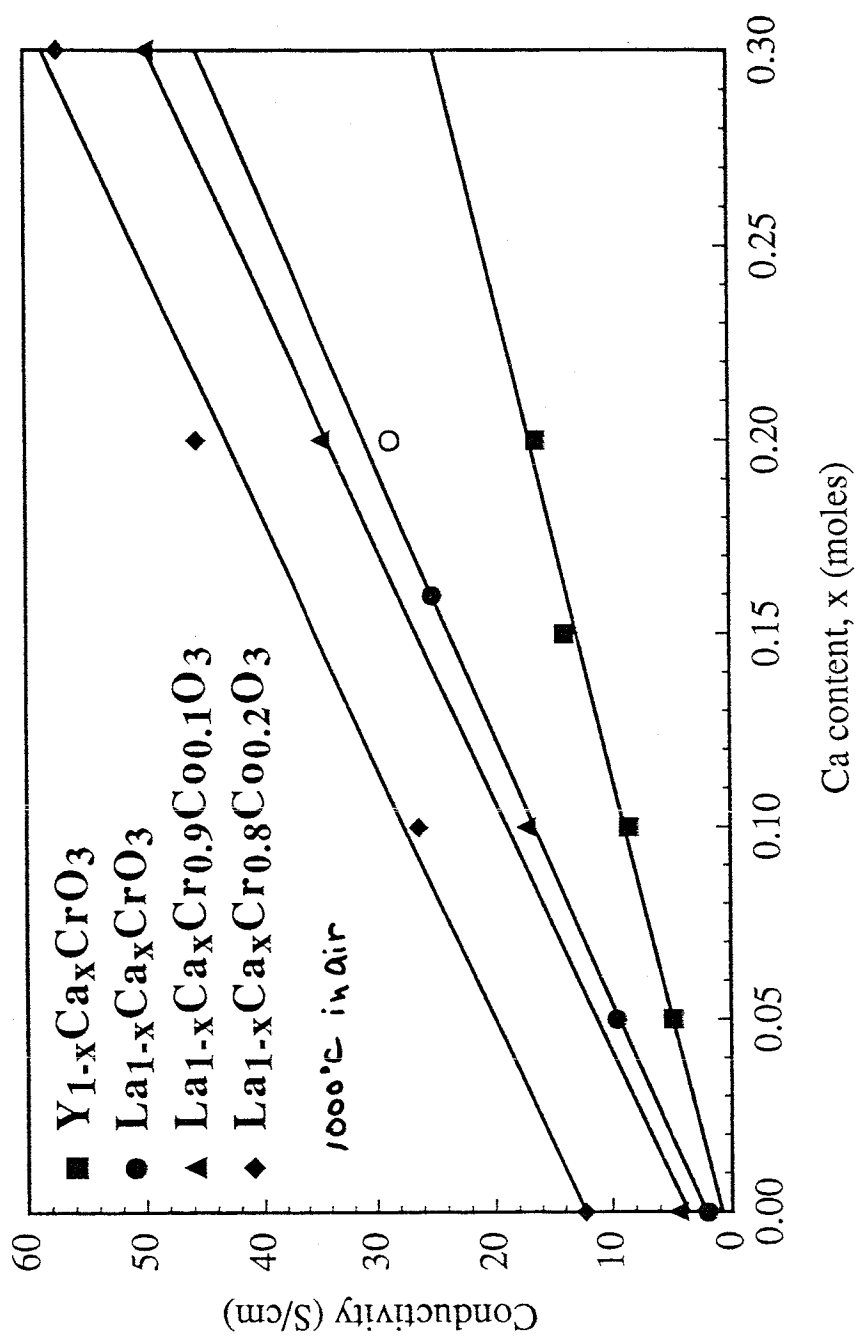


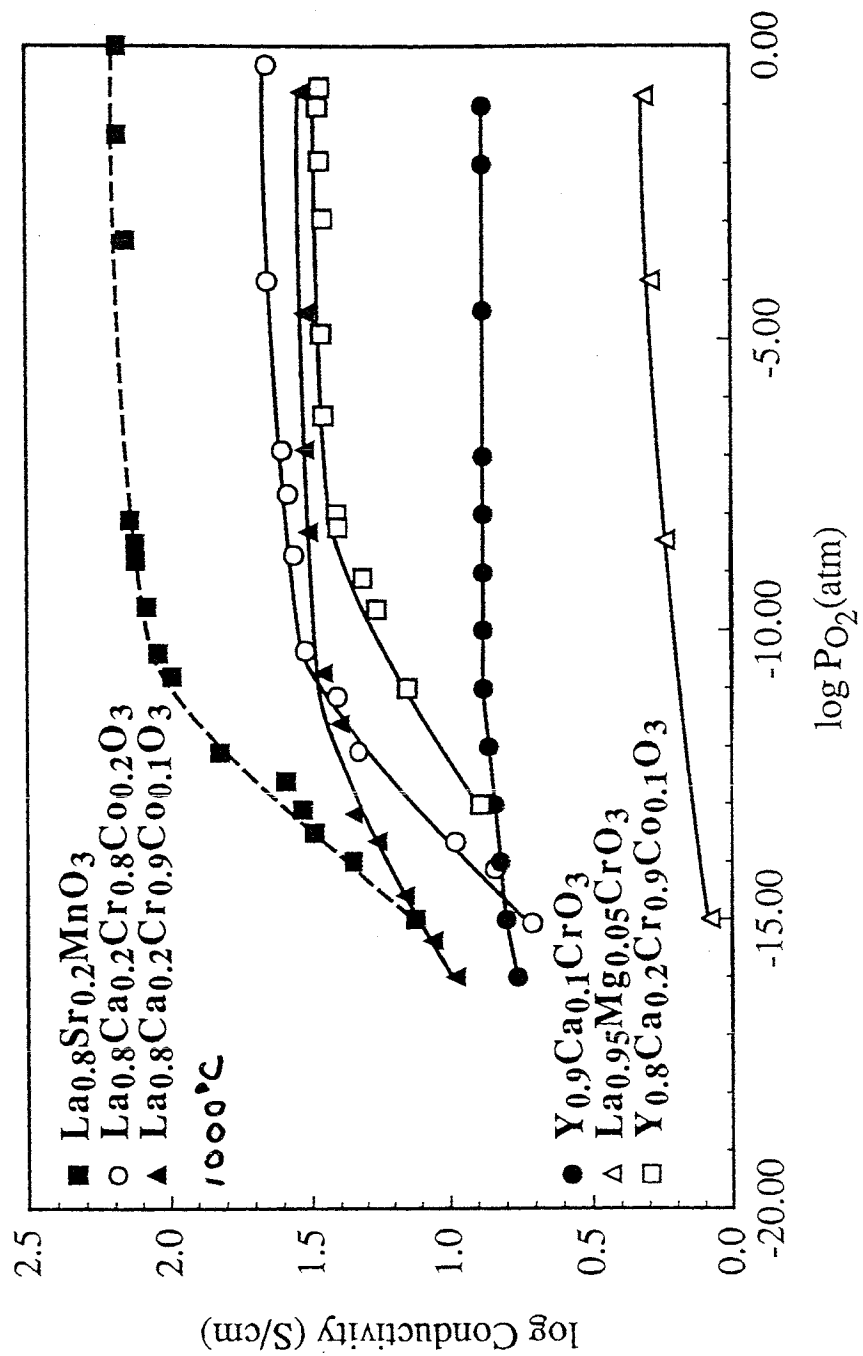
Y_{0.9}Ca_{0.1}Cr_{0.7}Li
Sinked to
1370°C
Furnace Cool

Table I. Thermal Expansion Coefficient (TEC) of LaCrO_3 and YCrO_3 as a Function of Ca and Co doping Between 100-1000°C.

Composition	TEC* ($\times 10^{-6}/^\circ\text{C}$)	Composition	TEC ($\times 10^{-6}/^\circ\text{C}$)
Undoped LaCrO_3	9.5	Undoped YCrO_3	7.8
10 % Mg doped LaCrO_3	9.5	10% Ca doped YCrO_3	9.4
2% Sr doped LaCrO_3	10.2	20% Ca doped YCrO_3	9.6
10% Co doped LaCrO_3	13.1	10% Ca, 10% Co, YCrO_3	10.1
20% Co doped LaCrO_3	13.6	20% Ca, 10% Co, YCrO_3	11.8
10% Co, 10% Ca, LaCrO_3	12.3	10% Ca, 20% Co, YCrO_3	12.3
10% Co, 20% Ca, LaCrO_3	11.1	10% Ca, 30% Co, YCrO_3	12.9
10% Co, 30% Ca, LaCrO_3	10.4	YSZ	10.3

*5% Standard deviation.





INTERCONNECT

CHALLENGES

- *Stability within Entire P_{O_2} Range*
- *Dense Micro Crack Free*
- *No Interactions*
- *High Conductivity*
- *Matching TEC*
- *Sinterable in Air at Temp. not Exceeding 1200°C*

CONCLUSIONS

- *Interfacial Polarization Eliminated by Developing Mixed Conductors.*
- *Novel Cathode Compositions Prepared with Tailored Physical and Chemical Characteristics.*
- *Buffer Layer Introduced to Prevent Interactions and Minimize Losses.*
- *Interconnect Compositions Developed with Superior Properties and Allow Co-sintering of Cell components in Air at 1200°C.*
- *Developed Materials Enabled SOFC Operation at 800°C*
- *A Novel Liquid Mix Technique was Developed for Syntheses of Cell Components.*
- *Thin, compact, Defect-Free Films where Developed Using a Novel Spin Coating Technique.*
- *Production of Fuel Cell Bundles Proposed by using Multi Channel Matrix/Filler Extrusion Technique.*

SOFC Materials Research in the Atomic Energy Authority of Egypt

M.El-Sayed Ali

Fuel cell activities in the Materials Division, Nuclear Research Center, Atomic Energy Authority of Egypt, will be reviewed. The research activities have been carried out by the ceramics group in the Metallurgy Dept., where the materials of the ceramic solid oxide fuel cell SOFC were the subject of research and development. The research focused on planar SOFC, in which the anode has been used as a support for the stabilized zirconia thin layer. The research includes: powder preparation and forming method in order to be able to prepare SOFC anode with the required specifications, coated with a very thin and gas tight electrolyte layer.

Solid Oxide Fuel Cell Research and development in the AEA of Egypt

The research focused on the preparation of Ni/YSZ supporting anode where two methods of preparation are currently used:

1- Poreformer technique

2- Coat Mix technique

The results obtained showed comparable pore structure with the required porosity for the supporting anode.

In order to integrate a local material that could be extracted from an Egyptian mineral, a side project has been started to extract

zirconia from the Egyptian zircon supplied by the Egyptian Authority for Nuclear Materials.

The preliminary results showed that the Egyptian zircon has a high purity of about 98% and that the zirconia obtained from has a high purity as well.

The future objective is to prepare low cost solid oxide fuel cell that can work at lower temperature about 750 C. The following will be taken in consideration:

- 1- Integrating the local clay materials in the preparation of the porous support for the anode layer.**
- 2- Using thin layer electrolyte and cathode.**
- 3- Using electrolytes having higher ionic conductivity than the YSZ material -currently used- for example ceria doped with gadolinia.**

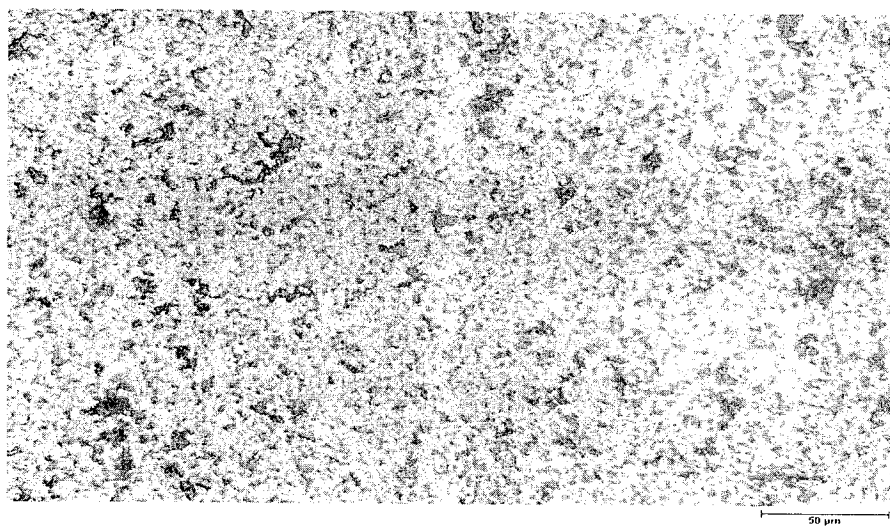


Fig. () Coat Mixing substrate

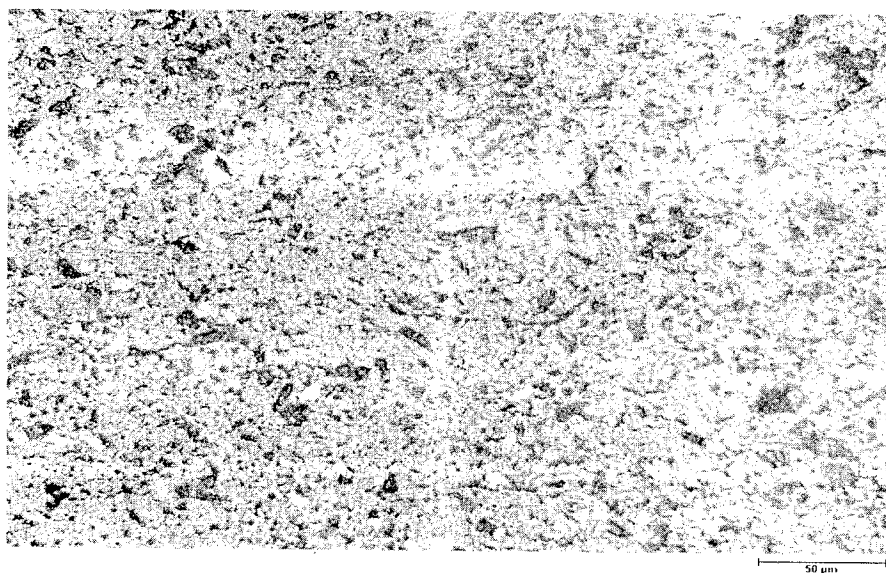


Fig. () Mechanical Mixing with pore former substrate

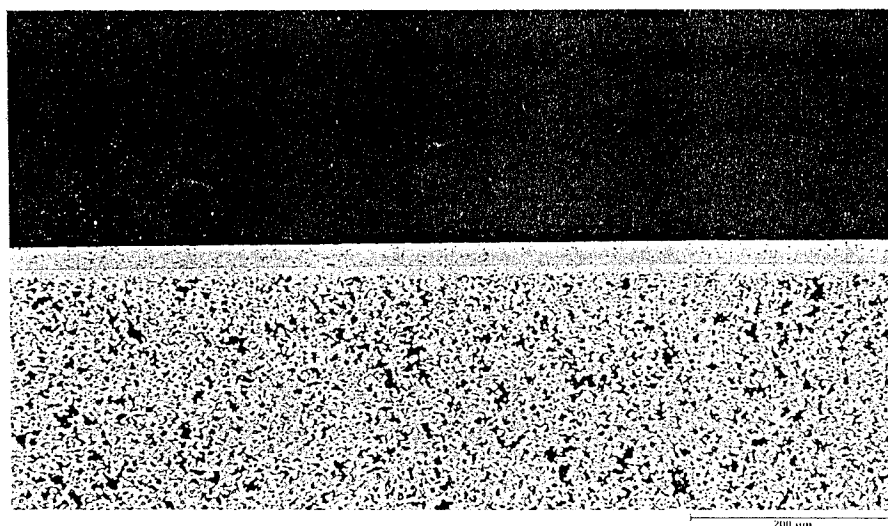


Fig. () Coat Mix substrate with functional and electrolyte layers applied by dipping method.

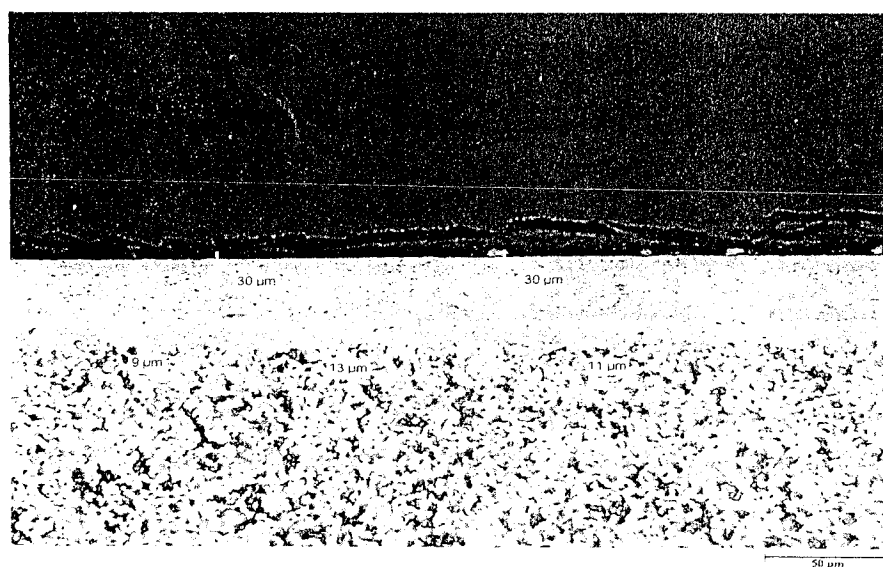
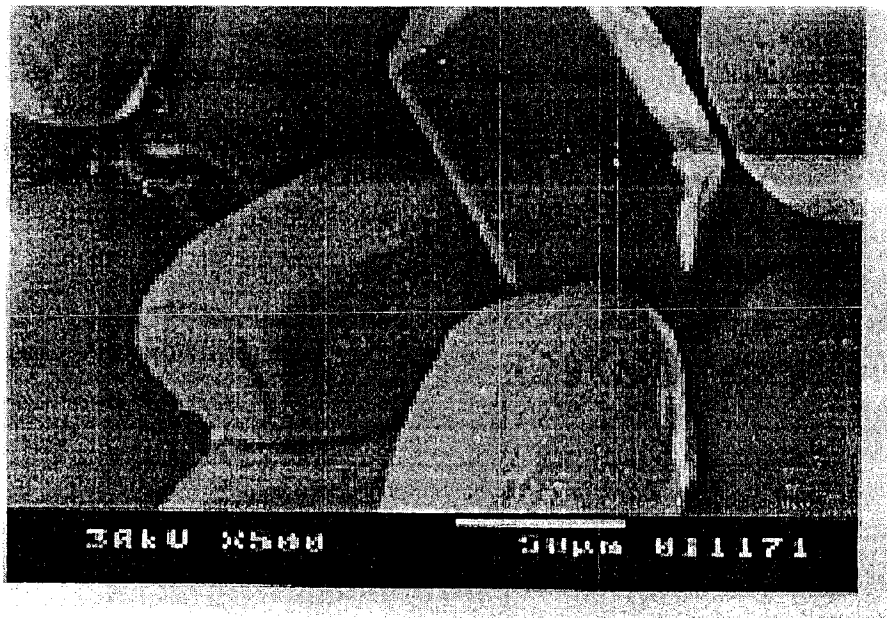
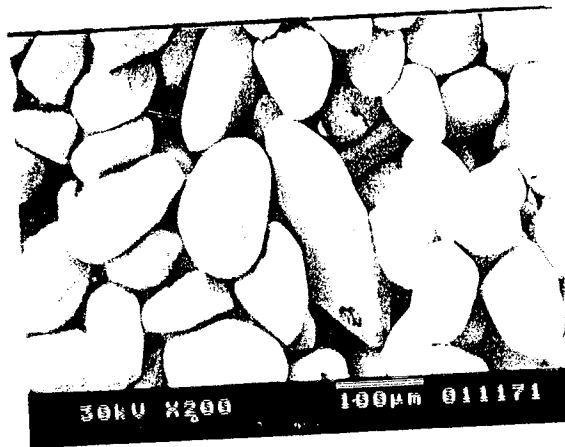
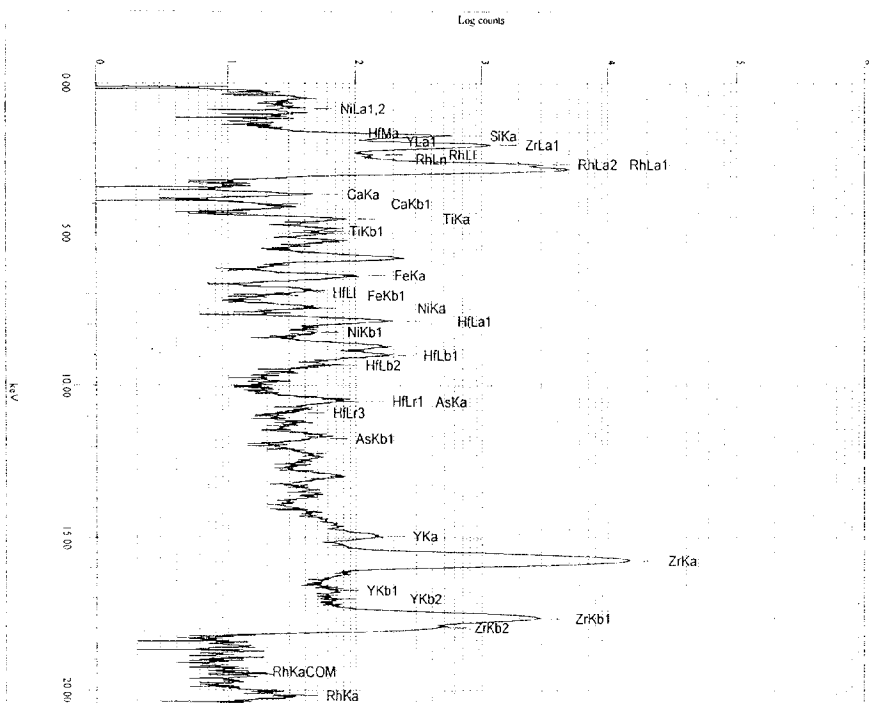


Fig. () Coat Mix substrate with functional and electrolyte layers applied by dipping method.





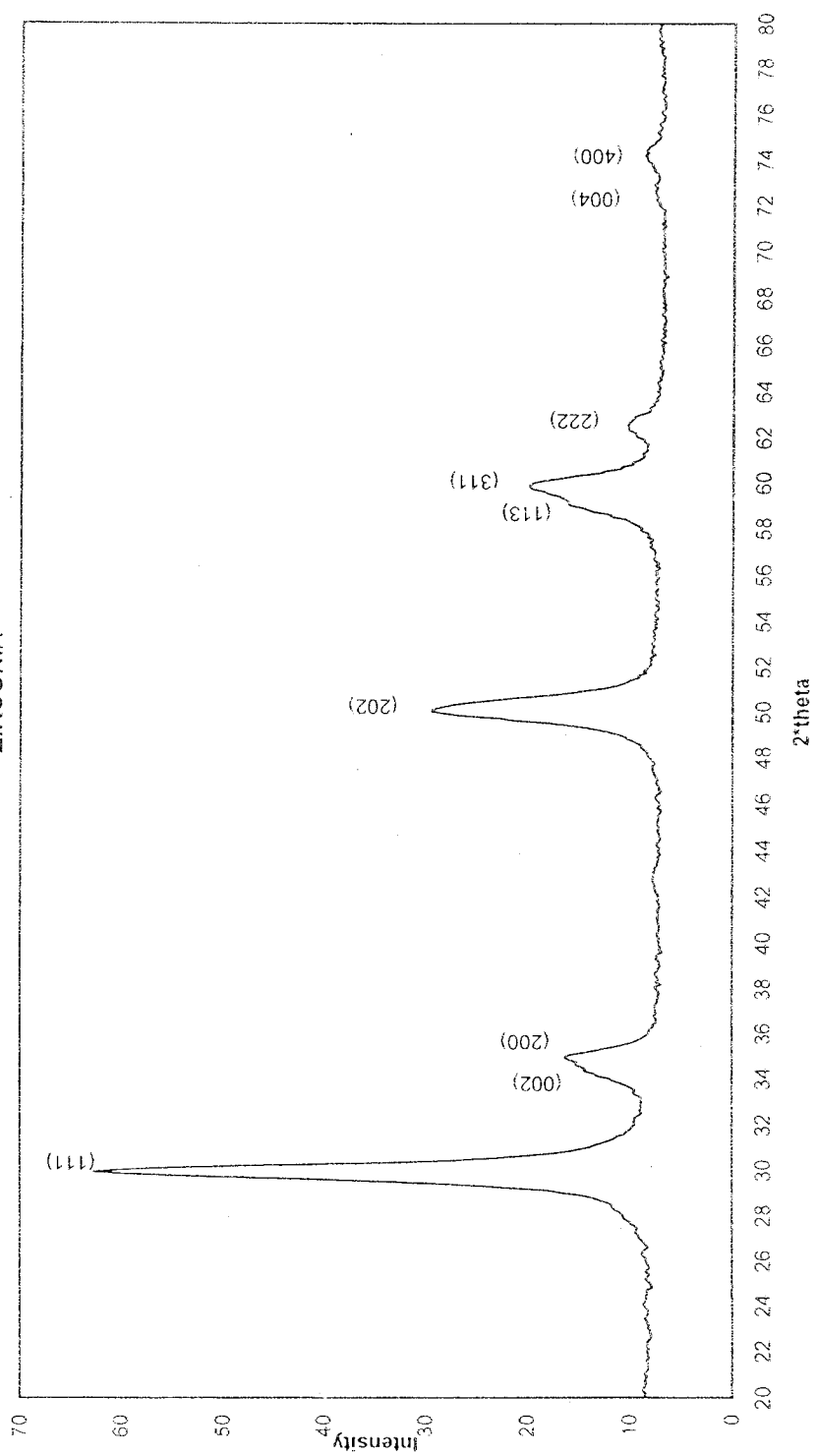
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 Memo :
 Acq. Cond.: Voltage: 30.0kV Current: 4.00mA Live time: 691.00sec Pass Vac
 Quantitative Analysis Condition
 Quantitative Analysis Method: Standard

Analysis Element: Si, Ca, Ti, Fe, Ni, As, Y, Zr, Rh, Hf

Num	Atom/Chem. Formula	wt(%)	at(mo) %
1	20 CaO	0.2917	
2	22 Ti	0.2278	
3	26 Fe2O3	0.2788	
4	28 Ni	0.0420	
5	33 As	0.0333	
6	39 Y	0.2145	
7	40 ZrSiO4	98.0758	
8	72 Hf	0.8341	

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ZIRCONIA



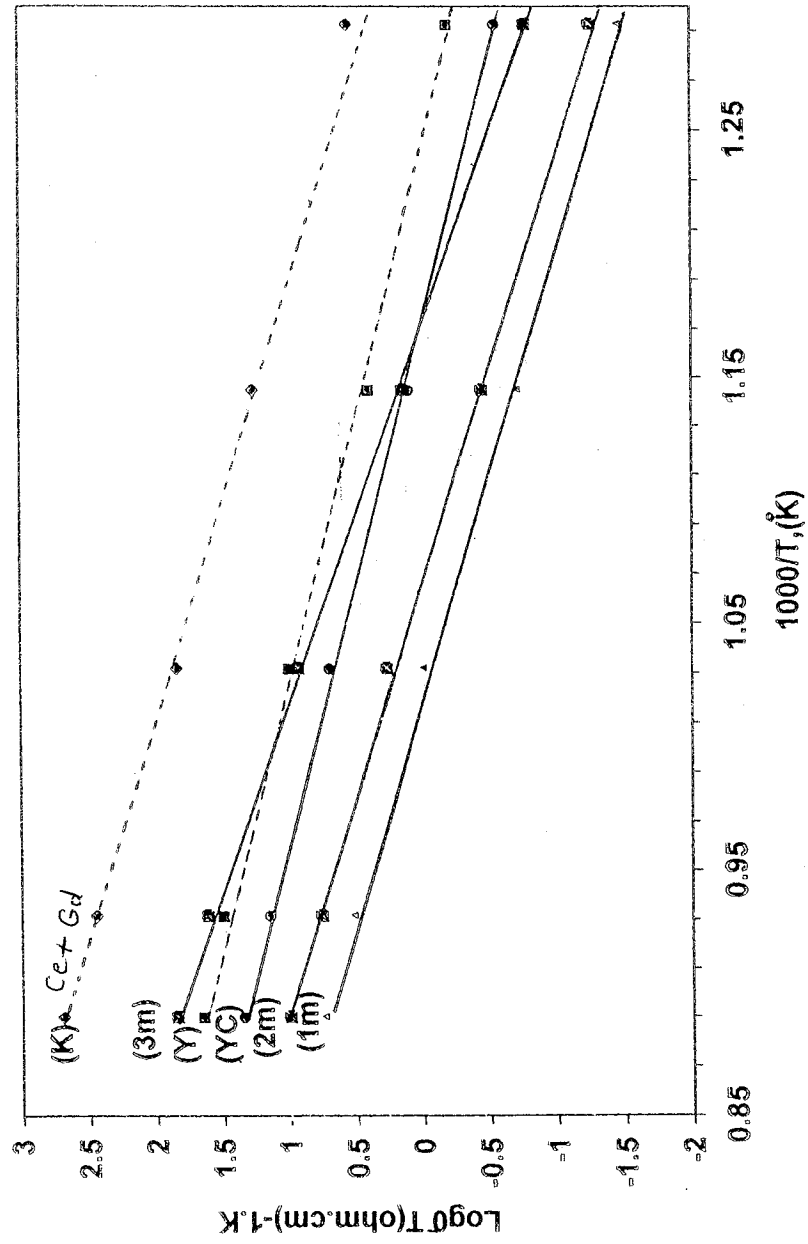


Fig. (45) :D-C electrical conductivity

Development of an optimized anode functional layer for SOFC application

A.A.E. Hassan*, N.H. Menzler, G. Blass, M.E. Ali*, H.P. Buchkremer, D.Stöver

*** Metallurgy department, NRC, AEA, Egypt.**

Abstract:

The development of optimized functional layers between the electrolyte and the electrodes of solid oxide fuel cells (SOFC) is of great interest. In this paper the effect of the anode functional layer with different thicknesses (2,5,8,16 μm) and different Ni content (40,45,50,55 vol.% Ni) on the performance of solid oxide fuel cell was investigated. The performances of cells with different anode substrates (S-mix and T-mix) were tested. The experiments show that, the performances of the cells with anode functional layer thicknesses of 2,5,8 μm and 16 μm are approximately the same. The cell with Ni content of 40 vol.% in the anode functional layer shows significantly better performance than the cells with higher Ni contents. The cell of (T-mix) substrate shows better performance than the cell of (S-mix) substrate especially at lower operating temperatures (750,800°C).

1. Introduction:

The main function of the Solid Oxide Fuel Cell (SOFC) anode is to provide the reaction sites for the electrochemical oxidation of the gas fuel. Thus, the anode material must be stable in the reducing environment and have sufficient electronic conductivity and catalytic activity for the fuel / gas reaction at the operating conditions. A porous cermet, made of Ni and Ytria stabilized zirconia (YSZ) is generally used as anode material. The network of Ni particles has a large catalytic activity and is responsible for transporting electrons from the electrode reaction site to the current collector. Open porosity is required for the electrode to supply fuel as well as removal of the reaction products. The addition of YSZ is necessary to support the Ni particles, to inhibit grain coarsening at the usual operating temperature and to give the cermet a thermal expansion coefficient acceptably close to that of the other cell components ⁽¹⁾. The presence of YSZ in the anode is considered to be inactive for the electrode reaction ⁽¹⁾. An alternative approach is that the YSZ component, extends the active area of the electrode reaction into the bulk of the electrode ⁽²⁾. Although sinterability of Ni is reduced with an increasing YSZ content, also increasing YSZ content raises IR resistance of SOFC. The particle size and ratio of Ni / YSZ are critical to the performance of the Ni/YSZ cermet anode ^(3,4). Deposition of a thin anode interlayer on the anode substrate with finer particles reduces the He-leak rate of the electrolyte and improves the cell performance ⁽⁵⁾. Another way to prevent the degradation of the anode could be by forming a graded multilayer anode, whose

diverse layers differ in their microstructure, to fulfill the locally different requirements for SOFC anodes. The first layer, which is adjacent to the electrolyte, consists of fine Ni and 8YSZ particles to provide a great electrochemical active surface as triple phase boundary (TPB). The thermal expansion coefficient (TEC) of this layer should be close to that of the electrolyte. The second layer, which is in contact with the electrical interconnector, should have a high electronic conductivity and high porosity for fast gas diffusion. A third transition layer is laying in between of these two layers. This transition layer has an intermediate composition and intermediate particle size compared to the other layers. Therefore the Ni content and the Ni particle size increase from the first to the second layer⁽⁶⁾. It was found that the IR resistance is sensitive to the contact area of Ni with the electrolyte. Polarization resistance is strongly affected by the Ni/YSZ ratio. So the double layer anode which consists of interfacial layer, using Ni rich cermet is effective in reducing IR resistance. The optimization of the anode interfacial layer needs much work⁽⁷⁾.

In the present study the effect of anode functional layer thickness, and the effect of different Ni content in the anode functional layer on cell performance was investigated.

II: Experimental Procedure:

1. Cell preparation:

Two types of supported anode substrate with standard composition (40 vol. % Ni) and different porosity, prepared by Coat Mix[®] process, were used. Two batches of binders were used in preparation process and are denoted as (S-mix. and T-mix.). An anode functional layer with different thicknesses of 2, 5, 8, and 16 μm were the first group of specimens, and a 5 μm anode functional layer with different Ni contents of 40, 45, 50, and 55vol.% were the second group of specimens. The anode functional layers were deposited on one side of S-mix substrate by modified slip casting process⁽⁸⁾. The deposited anode functional layers were calcined at 1000°C for an hour.

A thin layer of 5 μm thickness was applied on the calcined anode functional layer as electrolyte, using the modified slip casting process. The deposited layers were sintered at 1400°C for 5 hours. The He-leak test of the electrolyte layer was conducted at a different pressure of 100 mbar using He-Leak testing unit (Qualytest, Balzers).

Two cathode layers with a total thickness of about 60 μm were applied on the surface of the sintered electrolyte layer by the wet powder spraying (WPS) process⁽⁹⁾. The first cathode layer contains 40 wt.% YSZ and 60 wt.% LSM with fine particle size distribution ($d_{50}=0.3\mu\text{m}$). The second layer contains a coarser particle size of LSM ($d_{50}=0.5\text{-}0.7\mu\text{m}$). The cathode layers were calcined at 1100°C for 3 hour. The microstructures were investigated using a scanning electron microscope (LEO, 1530 gemini, Germany). The samples were

coated with a thin platinum film using sputtering device (BALZERS union, SCD 040, Germany).

2. Cell performance measurements:

The performance of a single cell was investigated using humidified hydrogen as fuel gas and dry air as oxidant. The cell was heated up in a furnace with programmable temperature controller to the operating temperature. The heating rate was 1K/min.. The anode was reduced using H₂/H₂O (88/12) gas mixture for several hours. The current-voltage measurements were measured using a HP6050A electronic. Potential and temperature data are collected using a PC-controlled Fluke NetDAQ system.

III. Results and discussion:

1. Effect of the anode functional layer thickness on the He-leak rate of the electrolyte layer:

The relationship between the anode functional layer thickness and the He-leak rate is shown in Fig. 1. The He-leak rate decreases with increasing the thickness of the anode functional layer from 2×10^{-5} to 3×10^{-6} mbar l/sec.cm² for an anode functional layer thickness 8-10 μ m. The leak-rate increases slightly to 4×10^{-6} mbar l/sec.cm² as the thickness of the anode functional layer increases to 16 μ m. This means that the tightness of the electrolyte layer is improved by increasing the thickness of the anode functional layer with an optimum thickness of about 10 μ m. The decrease of the leak rate may be due to the improved surface roughness of the anode functional layer.

2. Effect of the anode functional layer thickness on the cell performance:

Figures 2-5 show the I-V characteristic of a single cell at different operating temperatures with different anode functional layer thicknesses.

Table 1 summarizes the measured current densities of different cells with different thicknesses of anode functional layer, at a working voltage of one cell (0.7 V) and at different operating temperature. From table 1 it could be concluded that there was no noticeable change in the current density with increasing of the anode functional layer thickness from 2 μ m to 16 μ m. The data variations are in the range of a standard deviation.

3. Effect of the nickel content in the anode functional layer on the cell performance:

The performance of cells at different nickel contents in the anode functional layer is shown in Figs. 6-9. Increasing nickel content in the anode functional layer decreases the cell

Table (1) Current density of cells with different anode functional layer thickness at different operating temperatures.

Substrate	AFL thickness, μm	Electrolyte thickness, μm	Current density, A/cm^2 at different temperatures 0.7V, Hydrogen, Air!			
			750°C	800°C	850°C	900°C
S-Mix	2	5	0.55	0.65	0.95	1.05
S-Mix	5	5	0.50	0.65	0.90	1.10
S-Mix	8	5	0.48	0.65	0.80	1.00
S-Mix	16	5	0.56	0.58	0.84	0.87

Table (2) Current density of cells with different nickel content in the anode functional layer at different operating temperatures.

Substrate	Ni content in the anode functional layer, vol.%	Electrolyte layer thickness, μm	Current density, A/cm^2 at different temperatures 0.7V, Hydrogen, Air!			
			750°C	800°C	850°C	900°C
S-Mix	40	5	0.50	0.65	0.90	1.10
S-Mix	45	5	0.35	0.45	0.75	0.90
S-Mix	50	5	0.30	0.45	0.55	0.70
S-Mix	55	5	0.35	0.55	0.80	0.80

performance at the all-operating temperatures. The current densities measured at a working voltage of one cell (0.7V) and different operating temperatures are listed in table 2. As the nickel content in the anode functional layer increases up to more than 40 vol.% the current density measured decreases at all operating temperatures. The decrease in the current density may be due to the thermal expansion mismatch between the electrolyte layer and the anode functional layer containing a higher nickel content or due to agglomeration of the nickel particles.

4. Effect of porosity distribution in the anode substrate:

4.1. Substrate microstructure:

Figure 10 shows the surface microstructure of S-mix substrate and T-mix substrate respectively. The surface of T-mix substrate contains more wide and deeper pores than those of S-mix substrate, that may be a result of more agglomerations in the coated powder used for preparation of this type of substrate. After applying a 5 μ m thick of anode functional layer on the surface of the substrates, the surface of S-mix substrate is improved and the pores are closed as shown in Fig.11a. As for the surface of T-mix substrate, the pores are still open as shown in Fig. 11b. Applying another second layer of 4 μ m thickness on the surface of T-mix substrate the surface is improved and become better than the surface of S-mix substrate covered with a 5 μ m anode functional layer, fig. 11c. The He-leak rate measured for T-mix. substrate cell also improved by the applying of two anode functional layers and gives the same leak rate of cell with S-mix substrate.

Fig. 12a shows a polished cross-section of T-mix substrate without anode functional layer, after applying the first layer of anode functional layer using a suspension with fine particle size ($d_{50} = 0.3 \mu\text{m}$), the suspension is penetrated inside the substrate and there is no coherent layer formed (Fig. 12b). When the second layer was applied using the same fine suspension, the layer was formed (Fig. 12c). Using a coarser particle size suspension ($d_{50} = 0.9 \mu\text{m}$) in the first layer, the suspension did not penetrate inside the substrate and a layer was formed. The second layer was applied using the finer suspension ($d_{50} = 0.3 \mu\text{m}$) (Fig. 12d).

4.2. Cells performance:

Fig. 13 Shows the current-volt characteristic of a single cell of T-mix. substrate with double anode functional layers (two fine layers) and Fig. 14 shows the same characteristic with two layers (coarse + fine). At the working voltage of one-cell (0.7V) and at different operating temperatures, the current densities measured are shown in table 3.

From table 3, the current density obtained from the cell with T-mix substrate and double fine anode functional layers is slightly better than the current density measured by the other two cells. At an operating temperature of 800°C which is state-of-the-art in planer SOFC system the improvement is about 30% whereas at 900°C the current density is approximately the same.

Table (3) Current density of cells with different substrate and anode functional layers at different operating temperatures.

Substrate	AFL thickness, μm	Electrolyte thickness, μm	Current density, A/cm^2 at different temperature 0.7V, Hydrogen, Air!			
			750°C	800°C	850°C	900°C
S-Mix	5	5	0.50	0.65	0.90	1.10
T-Mix	5+4 (fine)	5	0.69	0.85	1.05	1.15
T-Mix	(3.5+3.5) (coarse +fine)	5	0.53	0.77	0.93	1.07

V. Conclusion:

- In the leak test ,the He-leak rate of the electrolyte layer decreases by increasing the thickness of the anode functional layer , it is lower than 5×10^{-6} mbar l/sec.cm² at 8 μm thickness. No change in the He-leak rate of the electrolyte is detected layer by increasing of the anode functional layer thickness to 16 μm .
- At the working voltage of one cell (0.7V) and at all operating temperatures (750, 800, 850 and 950°C), the cells with anode functional layer thicknesses of 2, 5 and 8 μm give approximately the same current densities. Whereas the cell with an anode functional layer thickness of 16 μm has a lower current density at 800°C.
- Increasing Ni content in the anode functional layer to be more than 40 vol.% reduces the performance of cell by reducing the current density measured at all operating temperatures.
- The cell with T-mix substrate and double fine anode functional layers has slightly better performance than the cell with S-mix substrate especially at 800°C .

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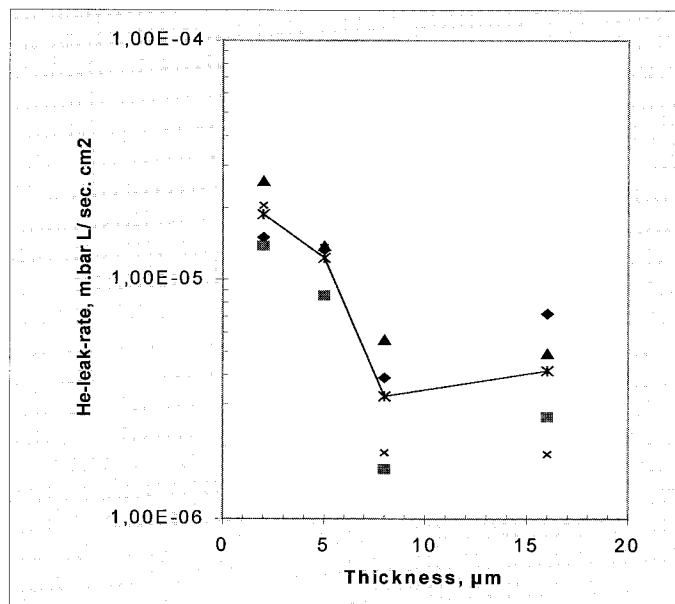


Fig. (1) Effect of anode functional layer thickness on He-leak-rate of cell.

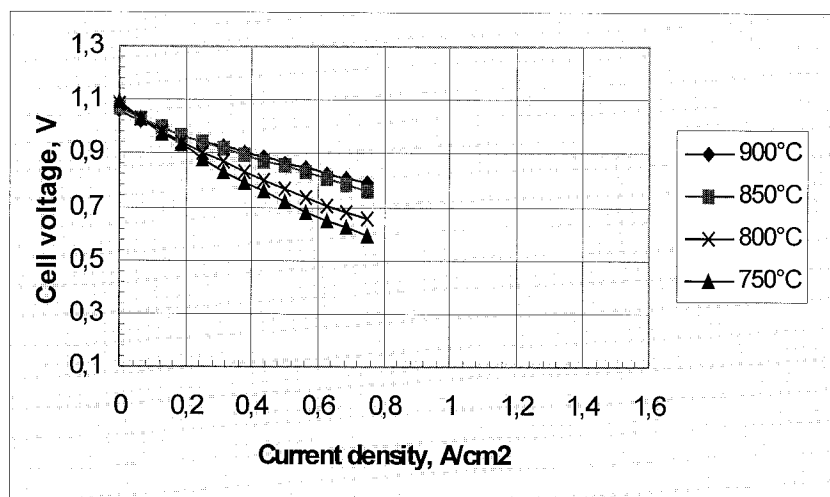


Fig.(2) Current-voltage characteristic of one-cell (40x40mm²) anode functional layer thickness 2µm.

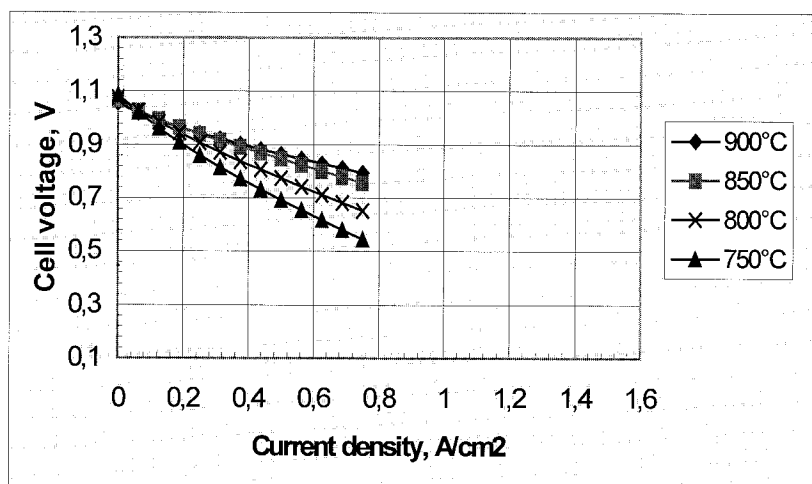


Fig.(3) Current-voltage characteristics of one-cell (40x40mm²) anode functional layer thickness 5µm.

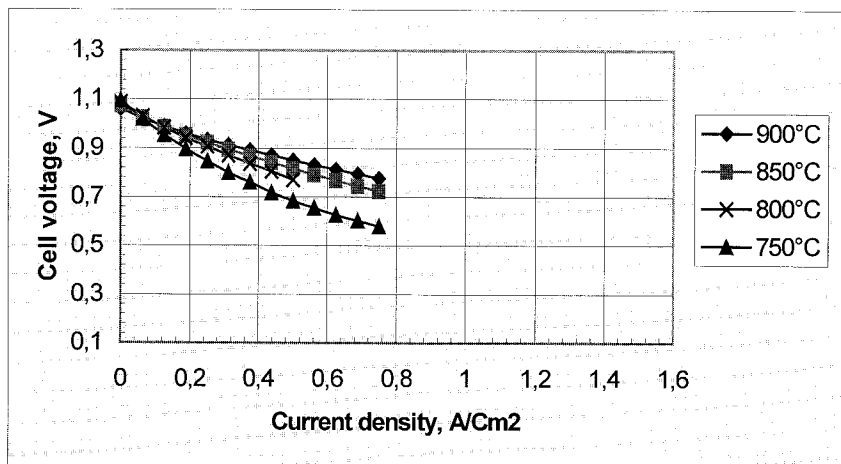


Fig. (4) Current-voltage characteristic of one-cell (40x40 mm²) anode functional layer thickness 8µm.

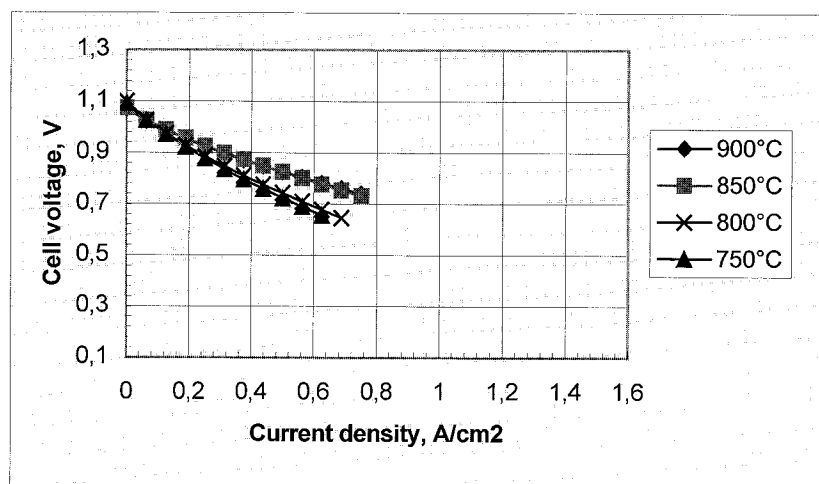


Fig. (5) Current-voltage characteristic of one-cell (40x40 mm²) anode functional layer thickness 16µm.

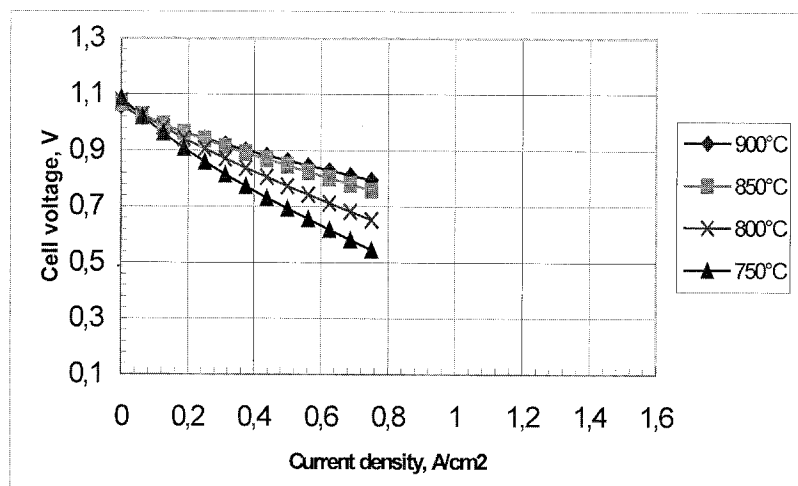


Fig.(6) Current-voltage characteristics of one-cell (40x40mm²) with anode functional layer contains 40 vol.% Ni

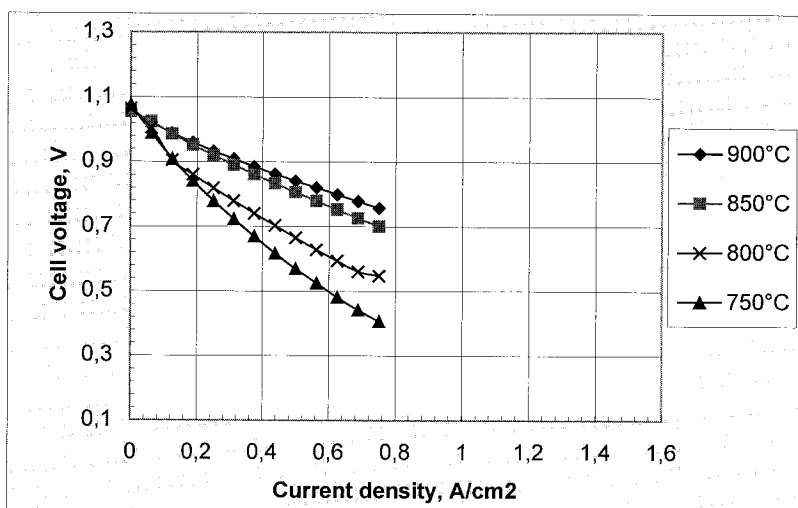


Fig.(7) Current-voltage characteristic of one-cell (40x40mm²) with anode functional layer contains 45 vol.% Ni.

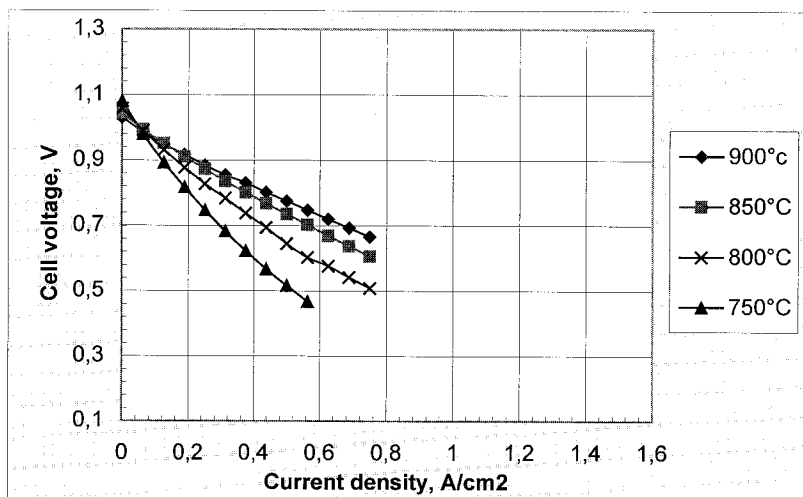


Fig.(8) Current-voltage characteristics of one-cell (40x40mm²) with anode functional layer contains 50 Vol.% Ni.

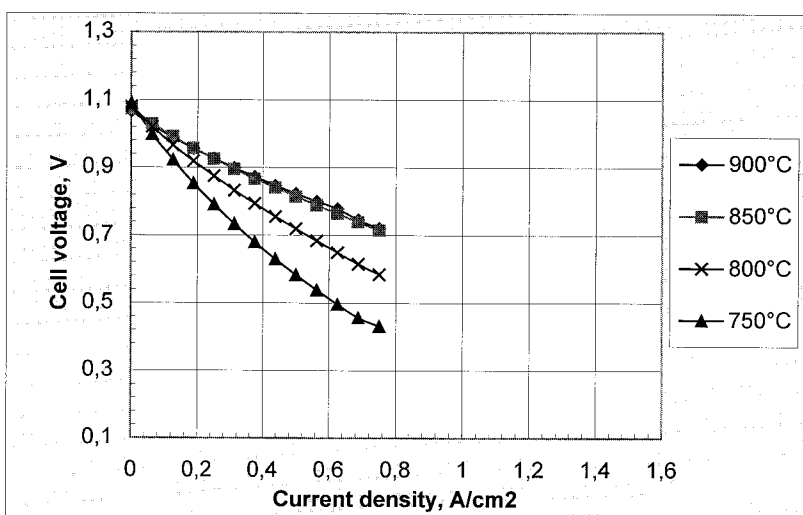
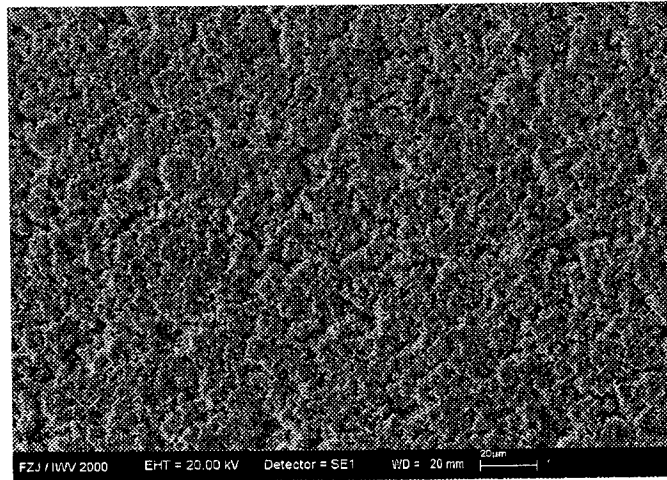
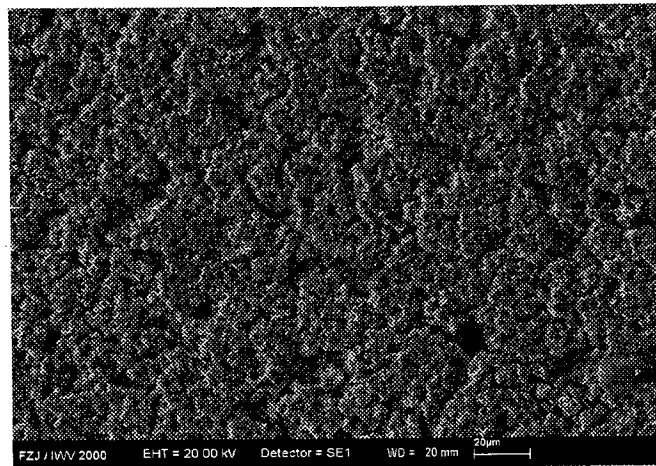


Fig.(9) Current-voltage characteristics of one-cell (40x40mm²) with anode functional layer contains 55 vol.% Ni.

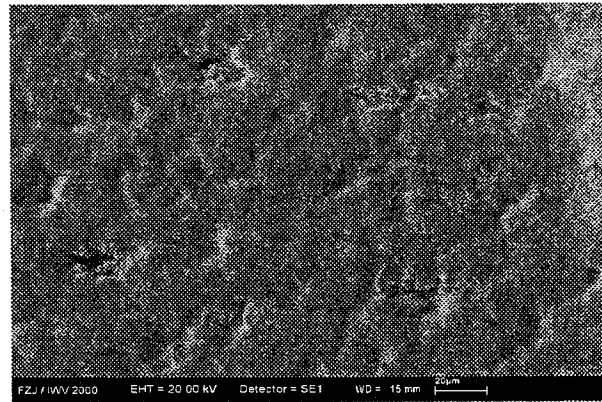


(a)

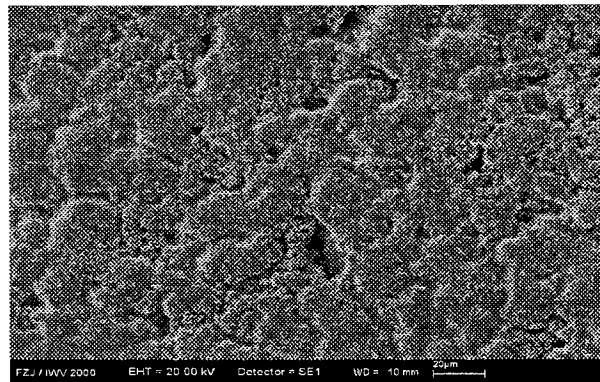


(b)

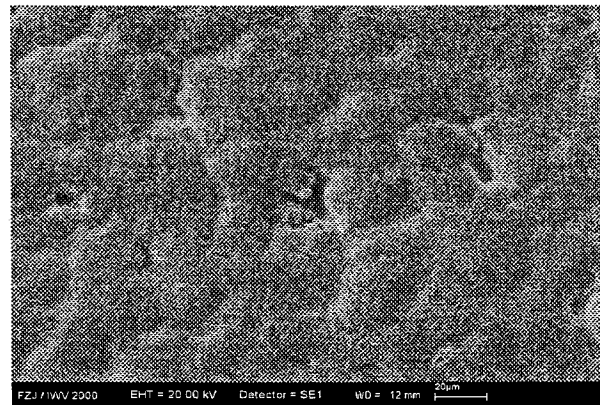
Fig. (10) The microstructure of the substrates surface, (a) S-mix. Substrate, (b) T-mix. Substrate (S,T are two patches of binder).



(a)

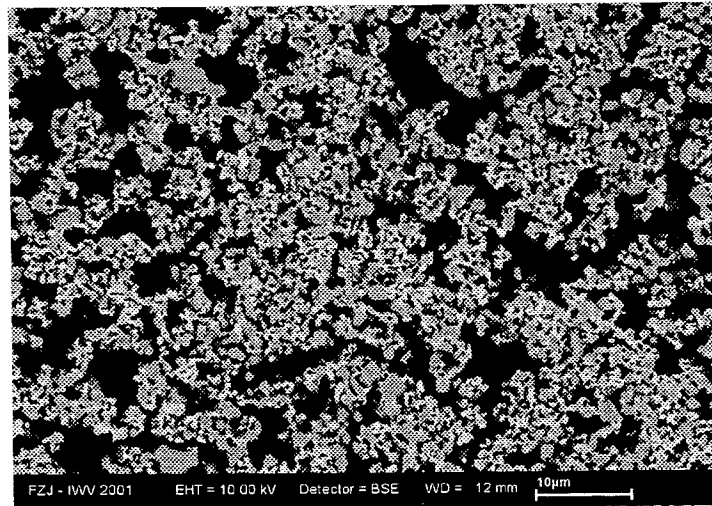


(b)

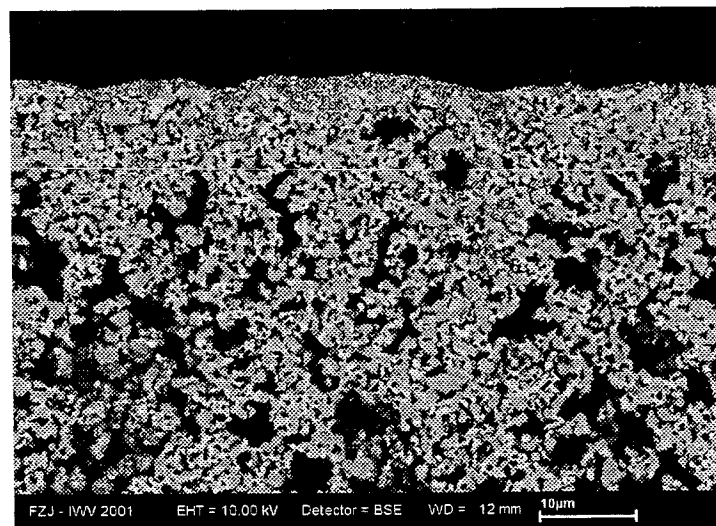


(c)

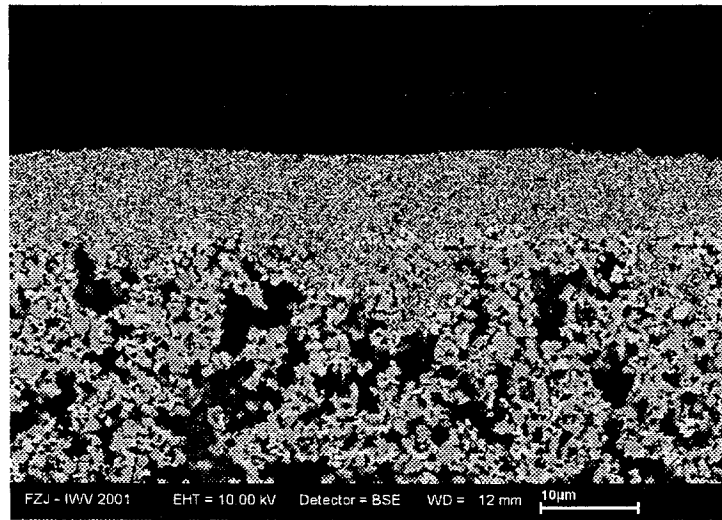
Fig.(11) The surface of the substrates with anode functional layers, (a) S-Mix, 5µm, (b)T-mix, 5µm and (c)T-mix two layers, 5µm each.



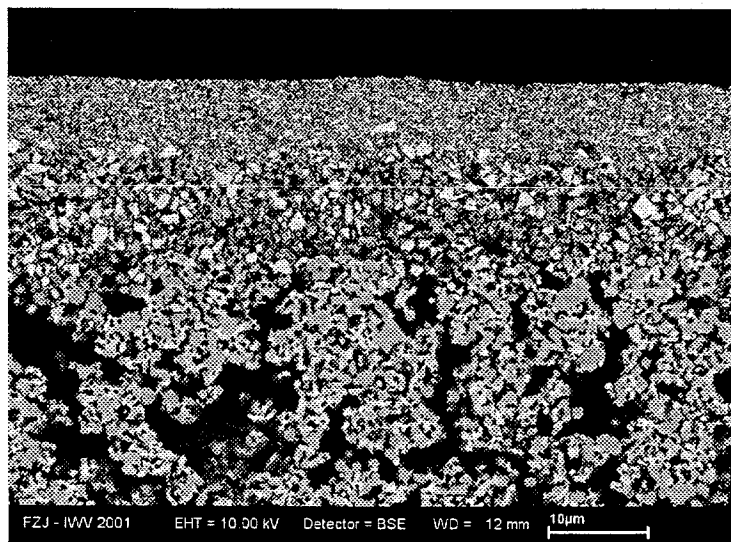
(a)



(b)



(c)



(d)

Fig.(12) Polished section of T.mix substrate, (a) without deposition,
(b) 5μm anode functional layer, (c) two fine layers
(d) two (fine +coarse) layers.

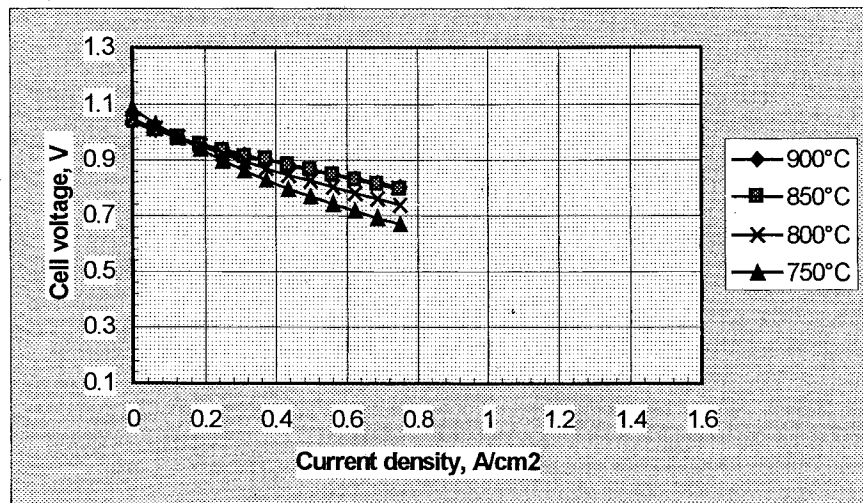


Fig. (13) Current-voltage characteristic of one-cell (40x40mm²) of T-mix substrate with double fine anode functional layers.

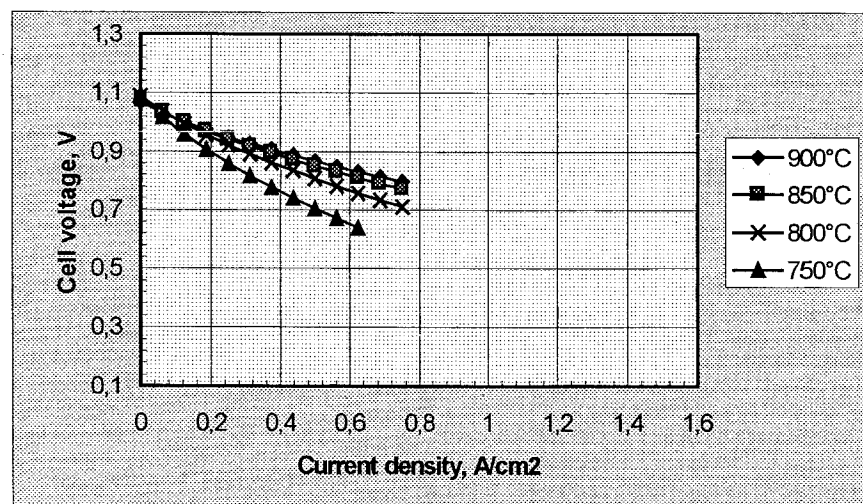
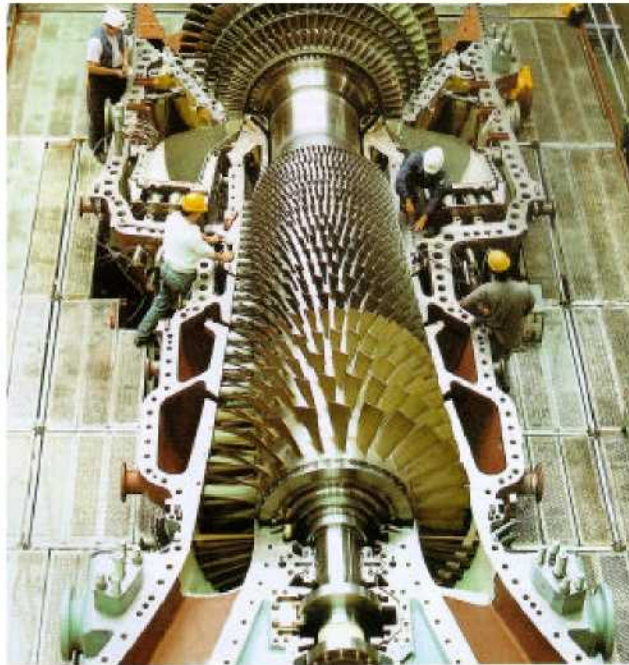


Fig. (14) Current-voltage characteristic of one-cell (40x40mm²) of T-mix substrate with double (coarse+fine) anode functional layers.

4. High Performance Materials



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High-strength cold formable steels for autobodies

Wolfgang Bleck

Department of Ferrous Metallurgy
Aachen University of Technology
Intzestraße 1, D-52072 Aachen, Germany

Abstract

Low alloyed multi phase steels are subject to extensive research efforts especially with regard to automotive applications due to their attractive combinations of mechanical properties. In this paper the microstructural characteristics differentiating multi phase steels from conventional cold formable steels are highlighted. The processing of dual phase steels and TRIP steels is described in detail and various alloying concepts are reviewed.

Introduction

For a great variety of applications the enhancement of strength remains one of the most important targets of material development. Economical and ecological considerations have even reinforced this tendency, as elevated strength levels are a prerequisite for light weight construction in the automotive industry which has gained increasing importance during the last years. To maintain or even strengthen the competitive position of steel for car body applications in spite of the distinctly higher specific weight in comparison with aluminum, magnesium, and plastic new material concepts have been developed and the maximum strength level of cold formable steels has been widely extended.

The conventional mechanisms to increase the strength in steel such as solid solution hardening or precipitation hardening are all based on an increase of the dislocation density or an increase of the different types of interactions with the dislocations. Unfortunately, in these cases the higher strength is accompanied by a noticeably inferior formability ([Figure 1](#)).

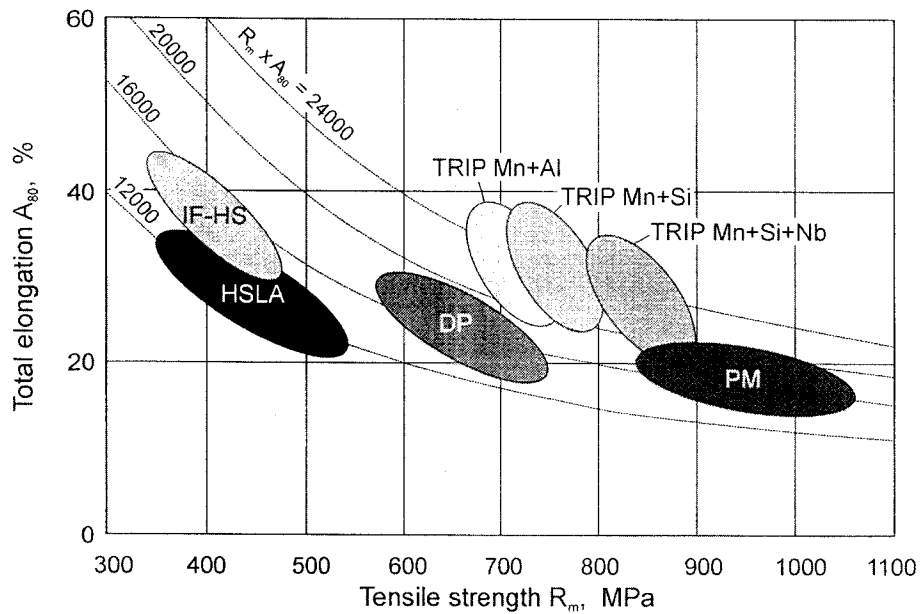


Figure 1: Ductility-strength relationship of several high strength cold rolled steels

The introduction of a new group of steels with a microstructure consisting of at least two different components has led to an enlargement of the strength level without a deterioration of ductility. The so called multi phase steels therefore offer very attractive combinations of strength and ductility which are due to the coexistence of the different microstructure components, their different mechanical behavior and their mutual interactions. The components of interest are regarded on the scale of light microscopy, i.e. with typical dimensions of a few micrometers. Multi phase steels can for example contain a relatively soft matrix phase being responsible for a low yield strength and a good formability along with a high tensile strength as a result of the presence of a hard second phase as in the case of dual phase steels. It is possible to vary the mechanical properties and to tailor them for the respective application foreseen by adjusting type, morphology and orientation and above all volume fraction, size and distribution of the different phases.

Additional potential for the improvement of mechanical properties can arise from the presence of a phase which does not represent an equilibrium constituent and which transforms during forming when the activation energy necessary is supplied. The transformation induced plasticity of so called TRIP steels associated with the transformation of face centered cubic austenite to body centered cubic martensite has a positive effect on both strength and formability. [Figure 1](#) provides an overview of the combinations of mechanical properties of various cold rolled high strength sheet steels including TRIP steels with different alloying concepts. Apart from the different levels of strength and ductility the flow

behavior of dual phase steels and TRIP steels shows characteristic differences to conventional cold formable steels namely continuous yielding in the first case and high uniform elongation and relatively low necking elongation in the second (Figure 2).

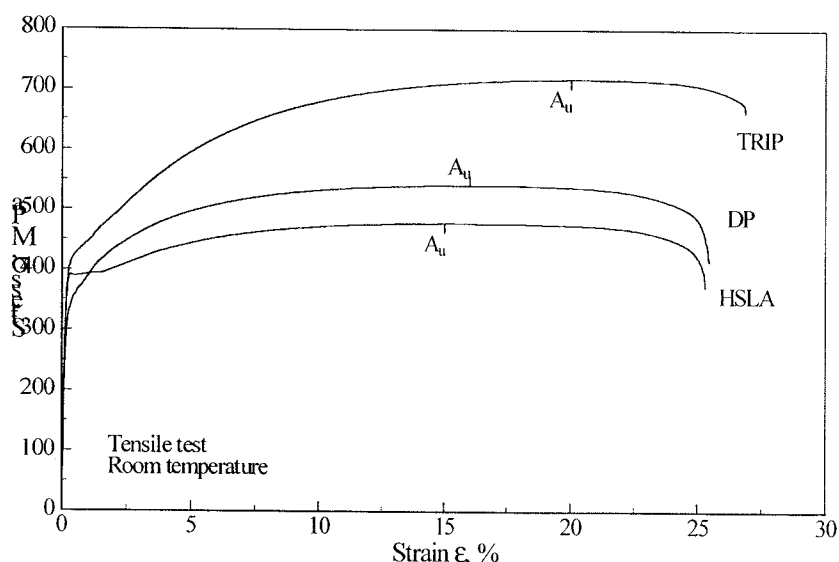


Figure 2: Stress-strain curves of high strength steels with approximately the same yield strength level and the specific features of different steel concepts

In this paper the physical background, important process parameters, and different properties of multi phase steels with low alloying levels for thin flat products are discussed.

Microstructural features of multi phase steels

The microstructure of multi phase steels is significantly different from single phase microstructures and therefore requires additional information such as volume fraction, size, distribution, and morphology of the different phases to be entirely described (Figure 3). Dual phase steels are characterized by small martensite islands in a ferritic matrix, while in duplex steels both phases are of the same order of magnitude with regard to amount and size. Duplex microstructures with austenite and ferrite components are of importance for stainless steels. TRIP steels are triple phase steels with two major fractions of ferrite and bainite and a minor fraction of retained austenite. In order to characterize this metastable microstructure component it is even necessary to procure data on the local chemical composition.

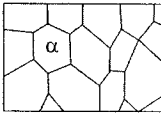
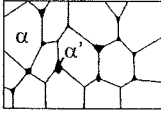
Steel type		Parameters	Phases
Single phase (Mild steel)		- Grain size - Grain shape	α = ferrite
Two phase (Dual Phase steel)		- Grain size - Volume fraction - Local chemical composition	α = ferrite α' = martensite
Two phase (Duplex steel)		- Grain size - Volume fraction - Local chemical composition	α = ferrite γ = austenite
Multi phase (TRIP steel)		- Grain size - Volume fraction - Local chemical composition - Phase stability	α = ferrite α_B = bainite γ_R = retained austenite

Figure 3: Microstructural characteristics of multi phase steels

Mechanical properties of different microstructure components of steel are compiled in [Figure 4](#). The data is based on literature as well as on experiments and can only serve as a first orientation, as the distribution of alloying elements between the components is usually inhomogeneous and as the properties strongly depend on the process parameters and especially the formation temperature of the microstructure components.

The formability of multi phase steels is above all determined by the ratio of yield stress and the volume fraction of hard and soft microstructure component. [Figure 5](#) provides an overview of the combination of these important parameters for several multi phase steels. Additional importance is ascribed to size and morphology of the constituents. The design of dual phase steels makes use of a small volume fraction of the second phase and a great difference in yield strength. Due to the generation of martensitic islands associated with volume increase and shape accommodation, localized dislocation accumulations and internal tensile stresses in the ferrite occur, which result in a low yield strength and a high strain hardening rate. For duplex steels, however, a good combination of strength and formability is obtained with similar volume fractions and yield strength levels of the two phases.

Phase	R_e , MPa	R_m , MPa	A, %	Hardness, H _v
Interstitial free ferrite	100 - 150	~ 280	~ 50	-
Ferrite (mild steel)	~ 220	~ 300	~ 45	-
Ferrite (0.7% Ni, 0.6% Cr)	~ 330	~ 550	~ 35	~ 180
Ferrite (13% Cr)	~ 300	~ 500	> 18	-
Pearlite	~ 900	~ 1000	~ 10	-
Cementite	~ 3000	-	-	800 - 1150
Nb carbonitrides	-	-	-	2500 - 3000
Bainite (~0.1% C)	~ 400 - 800	500 - 1200	≤ 25	~ 320
Martensite (~0.1% C)	~ 800	~ 1200	≤ 5	~ 380
Martensite (~0.4% C)	~ 2400	-	-	~ 700
Austenite (18% Cr, 8% Ni)	~ 300	~ 600	> 40	~ 240

- no data available

Figure 4: Characteristic mechanical properties of different microstructure components in steel; the figures indicate the approximate range of properties

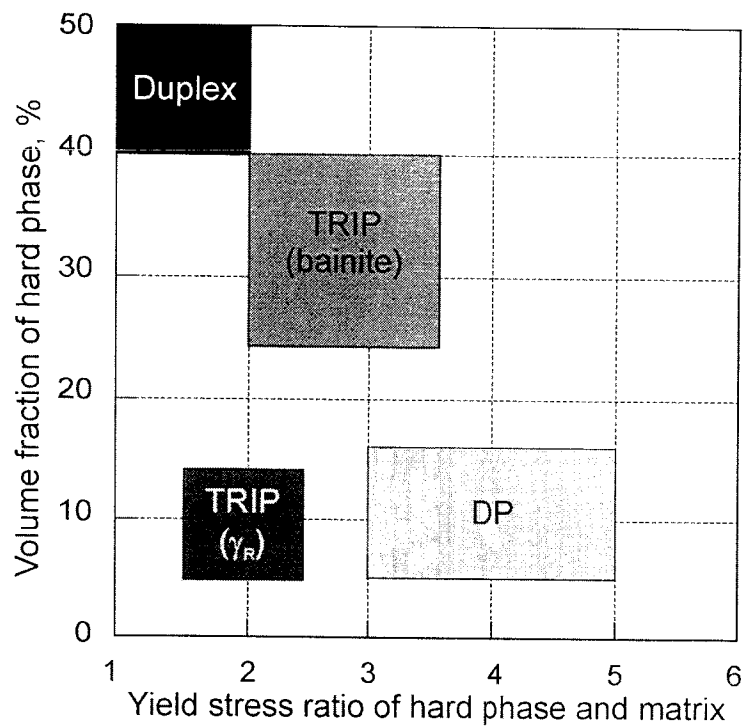


Figure 5: Volume fractions and yield stress ratios in multi phase steels

Processing of multi phase steels

Various process routes for dual phase steels and TRIP steels are either already in use or are subject to discussion depending on the product. [Figure 6](#) summarizes the different routes and demonstrates that hot rolled, cold rolled and galvanized end products can be produced for all of them. Other concepts of multi phase steels such as complex phase steels are not discussed in this paper.

Special attention has to be paid to the cooling strategy when producing hot rolled multi phase steels. After austenitization and the different steps of rolling in roughing and finishing mill the microstructure and the mechanical properties are finally adjusted in the cooling section consisting of runout table and coiler. A variation of the cooling intensity and the coiling temperature allows to change the transformation behavior and to vary the strength level in a wide range.

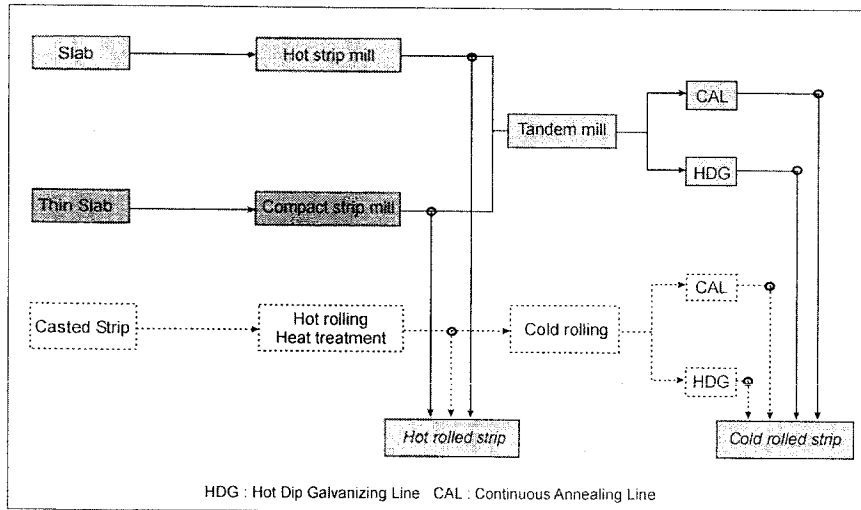


Figure 6: Process routes for hot and cold rolled multi phase steels

The temperature-time-schedule for the production of hot rolled dual phase and TRIP steels is presented schematically in [Figure 7](#).

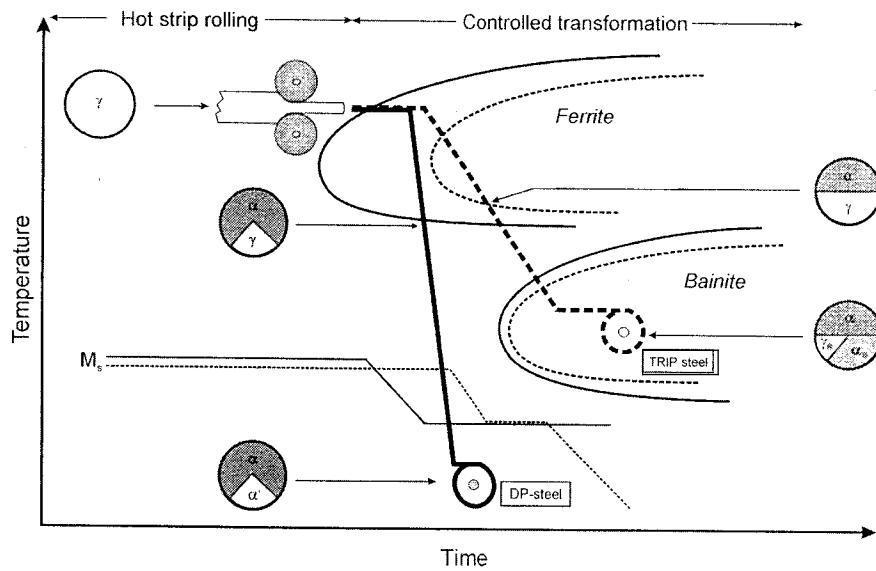


Figure 7: Temperature-time-schedule for hot rolled multi phase steels

The development of the desired microstructure might prove to be difficult as some transformations are necessary whereas others would be detrimental, which restricts the possible cooling path. Furthermore, the limited range of possible cooling rates on the runout table has to be taken into account. For dual phase steels the cooling rate must be low enough to enable the transformation of about 85 % austenite to ferrite to take place, associated with an carbon enrichment of the austenite, and at the same time high enough to avoid the formation of pearlite and bainite and to ensure the formation of martensite at low coiling temperatures of about 200 °C. Hence, a holding step has to be inserted in the temperature range of the maximum ferrite formation kinetics or the alloying concept has to be adapted in order to accelerate the ferrite formation.

For TRIP steels a lower cooling rate is applied, as ferrite formation is delayed due to the different alloying concept in general and the higher carbon content in particular and as the subsequent bainite is striven for. Coiling is therefore carried out in the temperature range of bainite formation at round about 500 °C and the final microstructure comprises 50 to 60 % ferrite, 25 to 40 % bainite, and 5 to 15 % metastable retained austenite that does not transform to martensite, since the carbon enrichment during ferrite and bainite transformation shifts the martensite start temperature below room temperature.

For cold rolled multi phase steels two different hot rolling approaches prior to cold rolling are conceivable first of them leading to a soft material with a microstructure of ferrite and pearlite. This microstructure stems from the application of a high coiling temperature of round about 700 °C. The material is well

suited for subsequent cold rolling. Alternatively, a hot rolling cycle making use of a lower coiling temperature in the range of bainite formation can be applied. As bainite forms at about 500 °C and represents a relatively hard microstructure component, distinctly higher rolling forces must be applied when cold rolling the material. However, it is expected that this process route leads to a more homogeneous and fine grained microstructure and superior properties of the as annealed product.

After cold rolling the sheet material has to undergo a heat treatment that can be realized in continuous annealing lines and in hot dip galvanizing lines. The volume fractions of the different phases of the final products are almost identical to those of hot rolled multi phase steels, but the respective microstructures are created in the course of completely different processes. Consequently, details such as the distribution of elements as well as precipitates in the phases and between the phases are most likely to differ from each other.

No full austenitization is performed during the heat treatment of dual phase steels ([Figure 8a](#)). An annealing temperature slightly above A_{c1} is applied and only a small part of 10 to 15 % of the microstructure composed of ferrite and pearlite or ferrite and bainite is transformed to austenite during this intercritical annealing. Afterwards the material is quenched and the austenite transforms to martensite during cooling to room temperature, so that the final microstructure consists of a dispersion of martensitic islands in a ferritic matrix.

TRIP steels are subjected to a two step heat treatment with intercritical annealing in the temperature range between 780 °C and 880 °C, cooling and another isothermal annealing between 350 °C and 450 °C which is then followed by cooling to room temperature ([Figure 8b](#)). The microstructure of TRIP steels after intercritical annealing contains almost identical percentages of ferrite and austenite, but in contrast to the microstructure of hot rolled TRIP steels the ferrite has been part of the microstructure prior to annealing and does not form during cooling from the intercritical temperature. Cooling is interrupted in the temperature range of bainite formation for several minutes, before cooling to room temperature is performed. During the second isothermal holding the austenite is mostly transformed to bainite thus leading to a final microstructure of approximately 50 % to 60 % ferrite, 25 to 40 % bainite, and 5 to 15 % retained austenite.

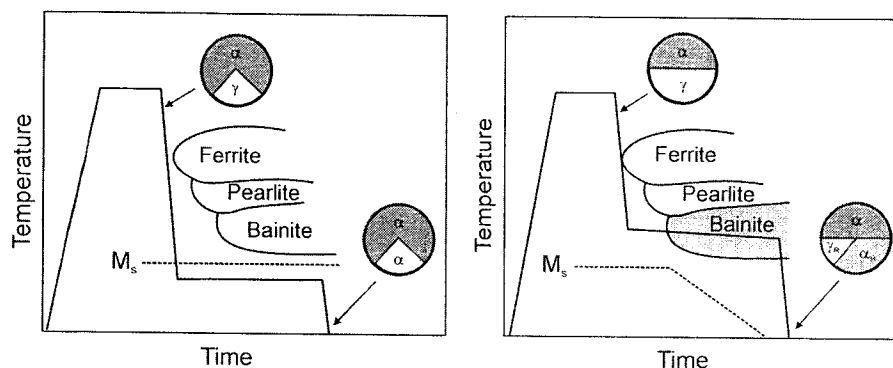


Figure 8: Temperature-time-schedule for cold rolled multi phase steels

The processes taking place during the various steps of the heat treatment of TRIP steels are listed in [Figure 9](#). The essential requirement is to transform part of the initial microstructure to austenite, to bring all carbon atoms in solid solution and to prevent any precipitation in the austenite, so that a sufficient amount of retained austenite with a sufficient carbon content is obtained. The significant role of niobium is hinted at and will be discussed in detail.

The description of the production process already implies the strict control of the process parameters which is necessary in order to produce the desired microstructure and mechanical properties. Hence, it is recommendable to produce multi phase steels on hot strip mills with a coil box, which ensures a defined cooling rate, a constant finishing temperature without use of a speed up, and a homogeneous temperature distribution over the strip width. [Figure 10](#) presents the demands that are characteristic of the production of multi phase steels, some drawbacks and handicaps, but also numerous advantages connected with the processing of dual phase and TRIP steels. For hot rolled products the combination of the improvements arising from a thermomechanical treatment and the benefits caused by multi phase behavior must be highlighted, for cold rolled material the possible production of high strength steels by the application of relatively low rolling forces is highly remarkable.

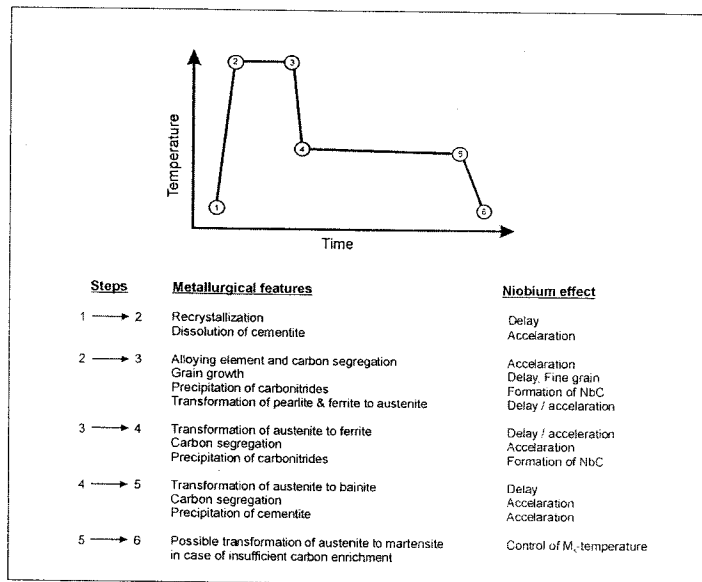


Figure 9: Metallurgical features during the processing of cold rolled TRIP steels

Hot rolled multiphase steels	Cold rolled multiphase steels
Benefits, Advantages ● Relatively easy processing in austenite phase ● Combination of thermomechanical treatment and transformation ● Easy control of microstructure and properties by variation of coiling temperature	Benefits, Advantages ● Relatively low rolling forces due to the soft hot rolled material ● Easy control of microstructure evolution in continuous annealing lines with two isothermal holding steps
Requirements, Prerequisites, Disadvantages ● Strong impact of temperature deviations on the transformation behaviour and thus on the properties ● Necessity of strict observance of the envisaged T-t-profile ● Necessity of homogenous distribution of the temperature among length and width of the strip ● Temperature speed up problematic ● Need for coilbox	Requirements, Prerequisites, Disadvantages ● Loss of the strength increase due to thermomechanical treatment ● Ideal conditions for austenite stabilization do possibly not coincide with industrially applied conditions ● Most applications require surface coating, which limits the range of possible chemical compositions

Figure 10: Comparison of the process routes of hot and cold rolled multi phase steels

Future aspects

The new developed high-strength steels combine good formability and a very high strength level, by this enabling the automotive user to design light-weight car bodies. These steels have been developed to cope with the challenge of lower density metals like aluminium and magnesium. The full exploitation of steel design can be obtained when these new steels are combined with new forming and joining techniques like hydroforming, laser welding and mechanical joining. They can be favorably used in tailored blanks, which are laser-welded blanks made from different sheets in order to optimize strength and thickness locally within an automotive component. It will be of great importance for the future prospects to develop computational tools to predict the material behaviour during forming, joining but also during performance in the car body.

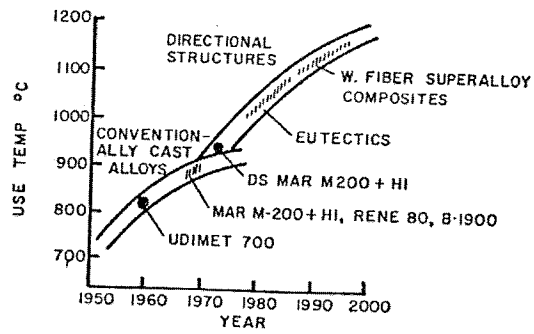
FIBER – REINFORCED COMPOSITE MATERIALS - AN OVERVIEW -

A. Y. KANDEIL

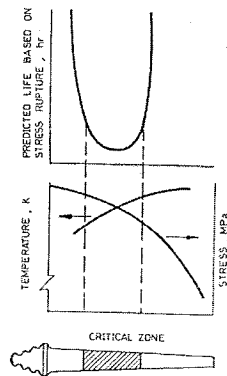
**Professor, College of Engineering and Technology
Arab Academy for Science and Technology**

OUTLINE:

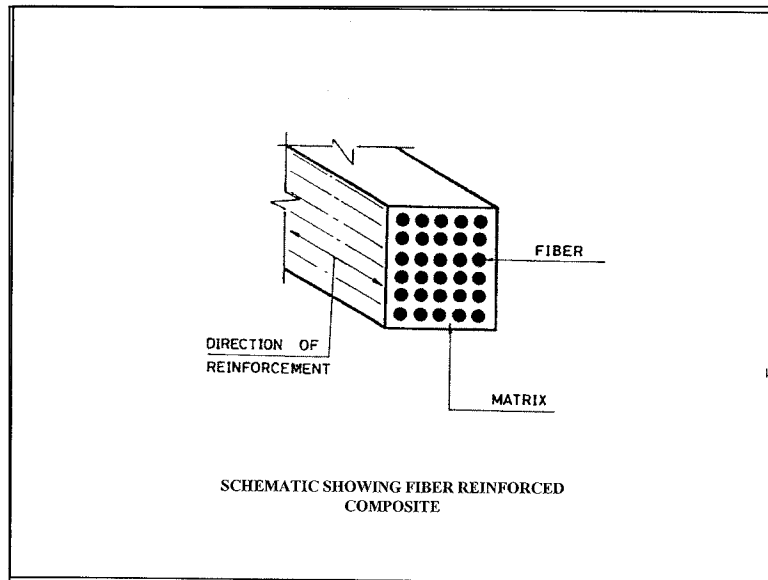
- INTRODUCTION
- FABRICATION METHODS
- FLOW AND FRACTURE BEHAVIOR
- FORMING LIMITS
- CONTROL VOID FORMATION
- CONCLUDING REMARKS



USE TEMP OVER PAST 50 YEARS FOR HIGH TEMP APPLICATIONS



TEMP AND STRESS DISTRIBUTION IN A TURBINE BLADE



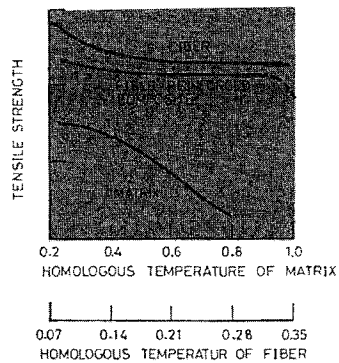
FIBERS

- VERY STRONG AND RIGID IN TENSION (DIRECTIONAL STRUCTURE, SIZE EFFECT)
- IMPROVE STRENGTH, STIFFNESS, CREEP, STRESS RUPTURE, ... etc
- SHORT (DISCONTINUOUS): ASPECT RATIO 20 TO 60
- LONG (CONTINUOUS): ASPECT RATIO 200 TO 500
- BORON, CARBON, GRAPHITE, GLASS, SILICON CARBIDE, SILICON NITRIDE, TUNGSTEN, STEEL, MOLYBDINIUM, ...etc

MATRIX

● THREE FUNCTIONS:

- SUPPORT AND TRANSFER THE STRESSES TO FIBERS
- PROTECT THE FIBERS AGAINST PHYSICAL DAMAGE & ENVIRONMENT
- REDUCE PROPAGATION OF CRACKS



SCHEMATIC COMPARISON OF TENSILE STRENGTH OF
COMPOSITE COMPONENTS AS FUNCTION OF HOMOLOGOUS
TEMPERATURE

APPLICATIONS OF ADVANCED FIBER REINFORCED COMPOSITES

- ADVANCED ENGINES FOR SUPERSONIC AIRCRAFTS
- TURBINES FOR HIGH-SPEED GROUND TRANSPORTATION
- ELECTRIC POWER GENERATION, HEAT EXCHANGER TUBES
- SPACE APPLICATIONS SUCH AS REENTRY SKIN STRUCTURES, ROCKET GUIDE VANES, ADVANCED ROCKET ENGINES, ...etc

MATERIAL REQUIREMENTS FOR ADVANCED COMPOSITES

- HIGH TEMPERATURE STABILITY
- TENSILE AND IMPACT PROPERTIES
- OXIDATION RESISTANCE
- CREEP RUPTURE STRENGTH
- THERMAL FATIGUE RESISTANCE
- DENSITY

FORMS OF INTERACTIONS BETWEEN FIBER AND MATRIX

- DISSOLUTION OF FIBER IN MATRIX
- CHEMICAL REACTION BETWEEN FIBER AND MATRIX
- RECRYSTALLIZATION OF FIBERS
- GRAIN BOUNDARY EMBRITTLEMENT OF FIBERS
DUE TO MATRIX DIFFUSION
- INTERNAL STRESSES RESULTING FROM THERMAL
EXPANSION MISMATCH BETWEEN FIBERS AND
MATRIX

APPROACHES TO MINIMIZE COMPATIBILITY PROBLEMS

- HIGH SPEED PROCESSING
- LOW TEMPERATURE PROCESSING
- DEVELOPMENT OF LOW REACTIVITY MATRICES
- APPLICATION OF DIFFUSION BARRIER (COATING)
- DESIGN TO MINIMIZE EFFECT OF REDUCED
STRENGTH

● COMPOSITE FABRICATION

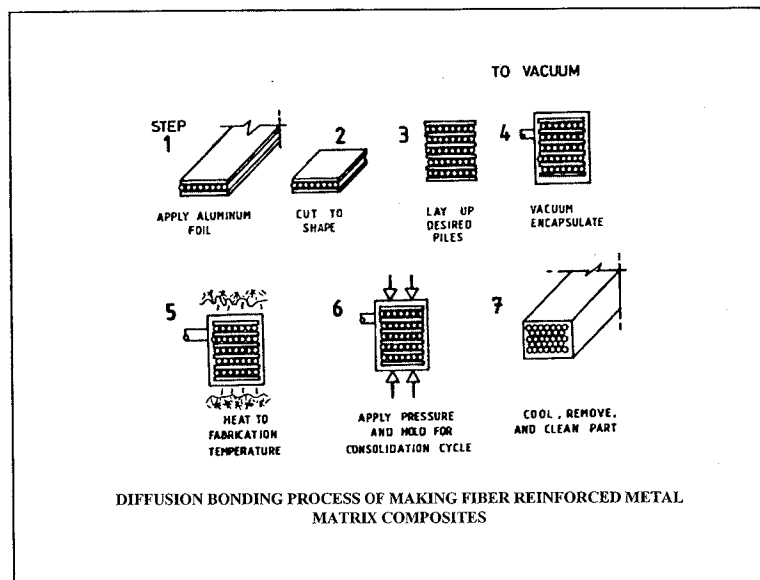
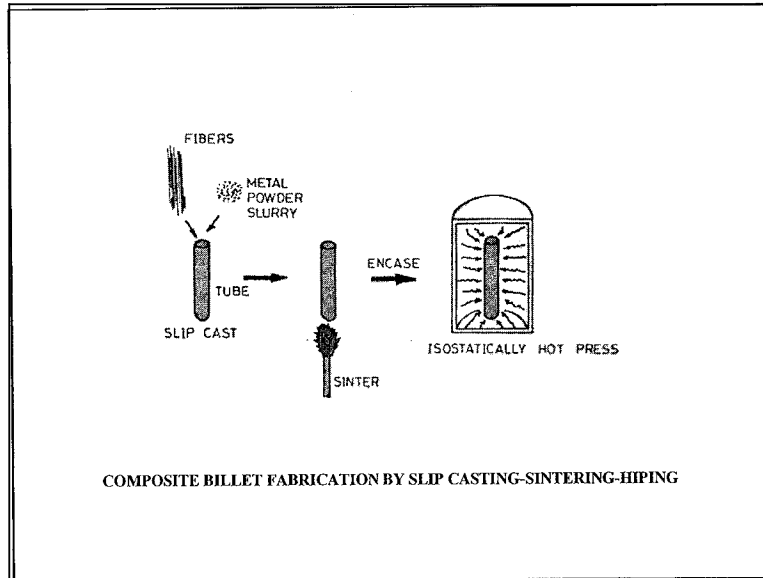
ACTUAL AND POTENTIAL COMPOSITE FABRICATION METHODS		
General Method	First Step	Consolidation
1. Powder Metallurgy	Pack fibers in matrix or slip cast matrix about fibers or use fugitive binder to hold fibers together	Sinter, hot press, hot isostatic press
2. Foil Metallurgy	Use fugitive binder or "glue" to bond fibers to foil.	Diffusion bond in hot press or hot isostatic press, brazing

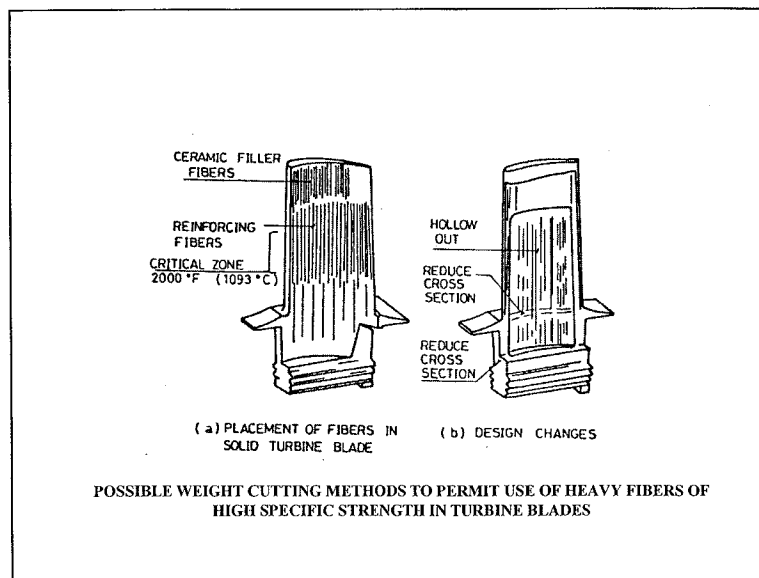
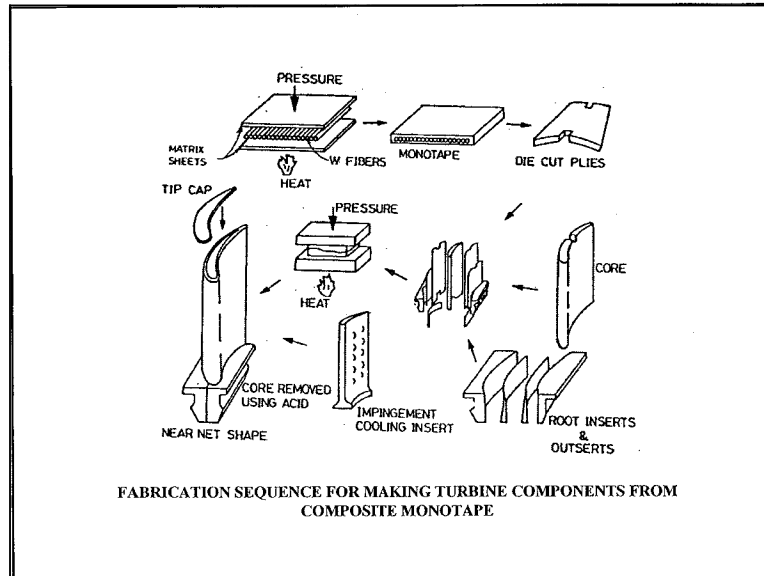
**ACTUAL AND POTENTIAL COMPOSITE
FABRICATION METHODS (cont'd...)**

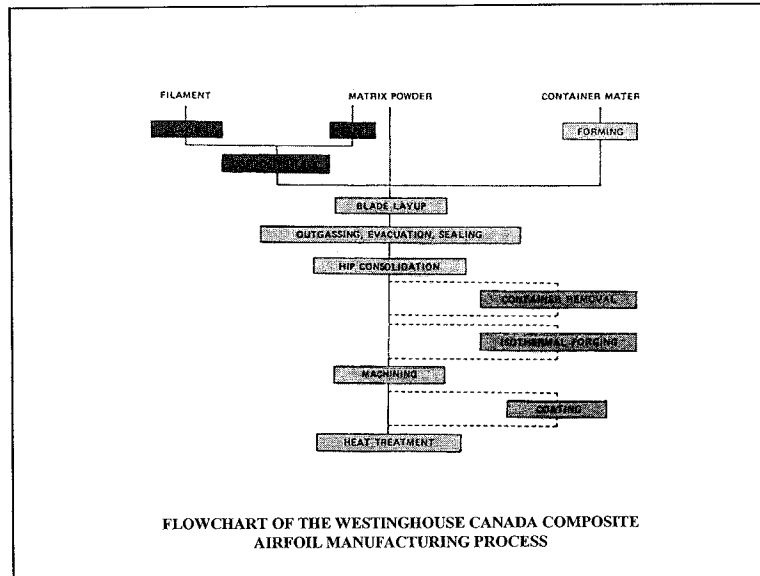
3. Casting	Cast entire part, cast matrix about fibers individual units or continuous types.	Non-when casting entire part continuous tapes- hot press or hot isostatic press
4. Electro- deposit	Electroplate or form shapes or types, electrophoresis	Hot press or hot isostatic press

**ACTUAL AND POTENTIAL COMPOSITE
FABRICATION METHODS (cont'd...)**

5. Vapor deposit	CVD, ion plates, vapor-ion beam	Hot press or hot isostatic press
6. Metal Spray	Pigma spray, molten metal spray	Hot press or hot isostatic press





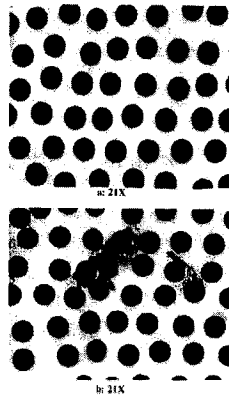


MATERIAL

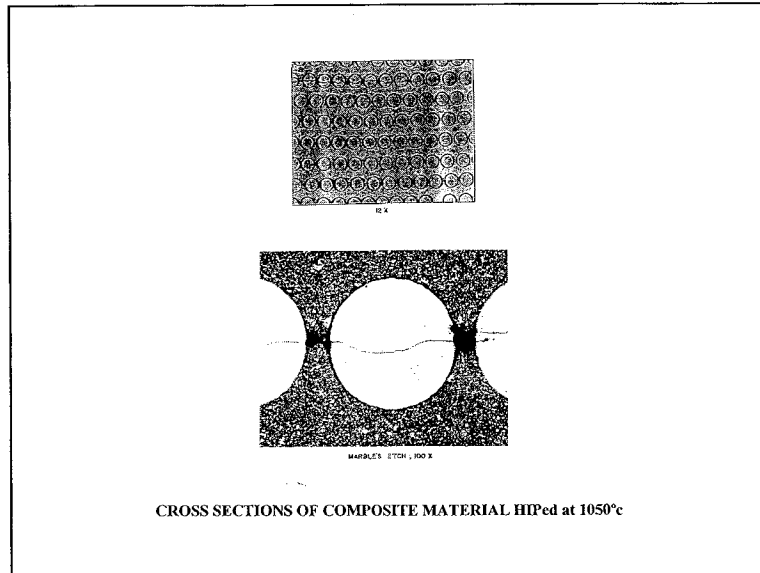
- Nickel – base superalloy
- Reinforced with 0.5 mm diameter high strength tungsten wires
- Vol. frac. ~ 40%
- HIP (1050, 1150°C; 103MPa for 2 hrs)

FORGING

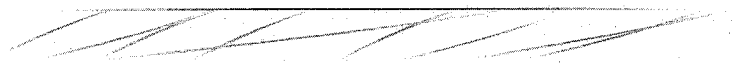
- Isothermal isostrain rate
- Subscale blanks 10 x 10 x 15 mm
- Loading was $\perp$ to fiber reinforced
- Temp between 1050°C and 1180°C and strain rate: to $10^{-1} - 10^{-5} \text{ s}^{-1}$



CROSS SECTION OF COMPOSITE MATERIAL
HIPed AT 1150°C



● FLOW BEHAVIOR



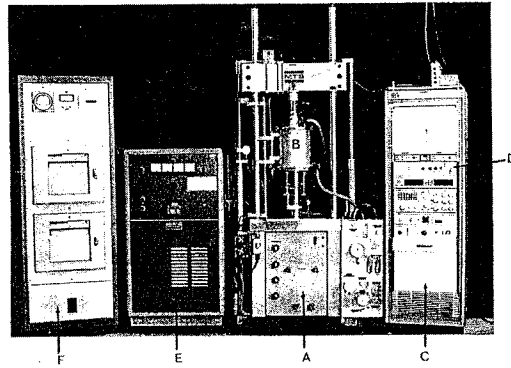
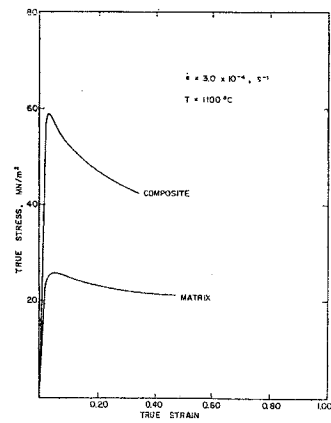
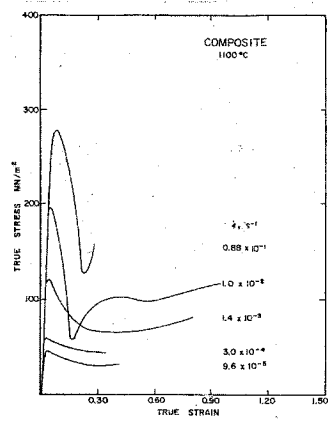


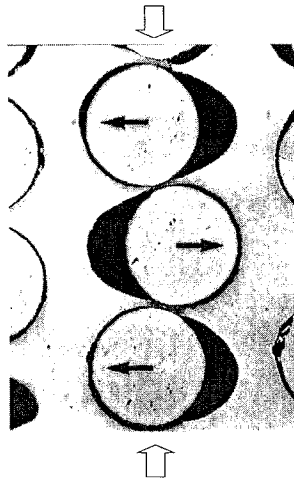
FIG. 2. LAYOUT OF INDUCTION HEATING COMPRESSION SYSTEM, SHOWING (A) MTS LOAD FRAME, (B) ENVIRONMENTAL CHAMBER, (C) MTS CONTROL SYSTEM, (D) EXPONENTIAL FUNCTION GENERATOR, (E) LEPEL INDUCTION GENERATOR, (F) TEMPERATURE CONTROLLER, RECORDERS



FLOW CURVES FOR MATRIX AND COMPOSITE MATERIALS PERFORMED AT $3.0 \times 10^{-3} s^{-1}$ AND $1100^{\circ}C$



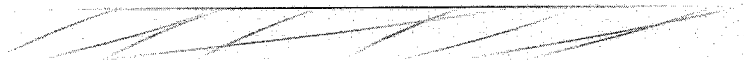
EFFECT OF STRAIN RATE ON THE FLOW CURVE OF
COMPOSITE MATERIAL AT 1100°C



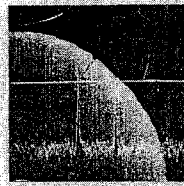
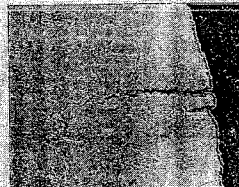
TRANSVERSE SECTION OF FORGED COMPOSITE SHOWING EXTENSIVE
CAVITIES DEVELOPED NORMAL TO THE LOADING DIRECTION AT THE
FIBER MATRIX INTERFACE.

SOLID ARROWS INDICATE THE DIRECTION OF FIBER MOVEMENTS

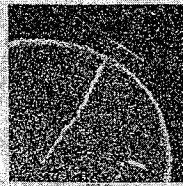
● FRACTURE BEHAVIOR



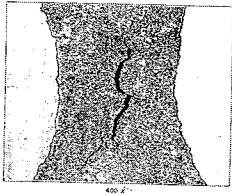
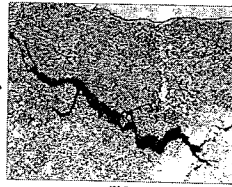
ELECTRON IMAGE OF
TUNGSTEN FIBER



X-RAY SCAN FOR HAFNIUM AT THE
LOCATION OF THE HORIZONTAL
TRACE



X-RAY IMAGE FOR HAFNIUM
SHOWING CONCENTRATION IN
THE CRACK



TRANSVERSE SECTIONS OF COMPOSITE MATERIAL SHOWING
MATRIX CRACKING DEVELOPED DURING FORGING TO 0.1 STRAIN
AT 1180°C AND $0.88 \times 10^{-4} \text{ s}^{-1}$

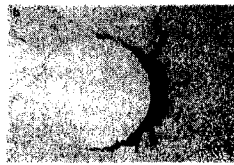


STRAIN=0.3
TEMP.=1100°C
STRAIN RATE= $0.88 \times 10^{-4} \text{ s}^{-1}$

TRANSVERSE SECTIONS OF COMPOSITE MATERIAL SHOWING
MICROVOIDS DEVELOPED AT POWDER PARTICLE BOUNDARIES DURING
FORGING

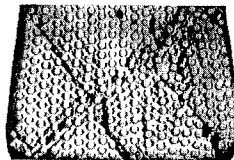


UNTCHED 300X



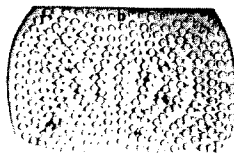
MARBLE'S ETCH; 300X

FRACTURE DEVELOPED AROUND COARSE PARTICLES IN MAR M200 COMPACT DURING HOT WORKING TO A STRAIN OF 0.6 AT 950°C AND $1.4 \times 10^{-3} \text{ S}^{-1}$



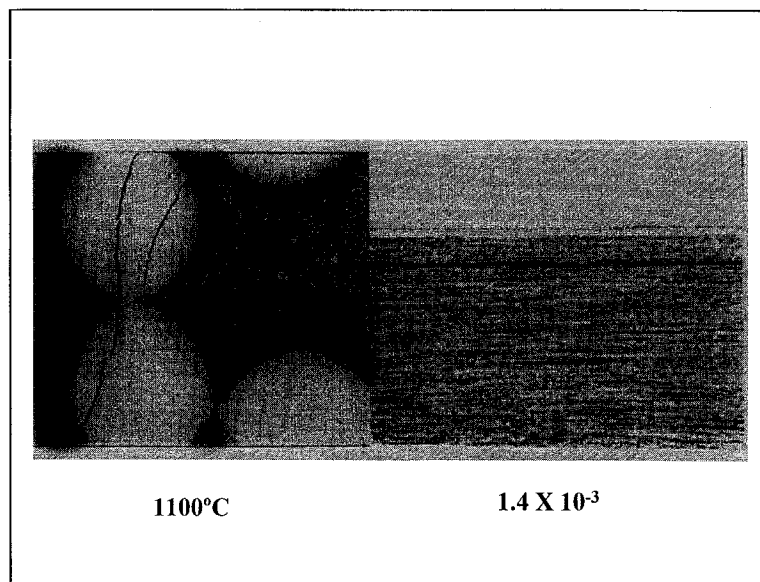
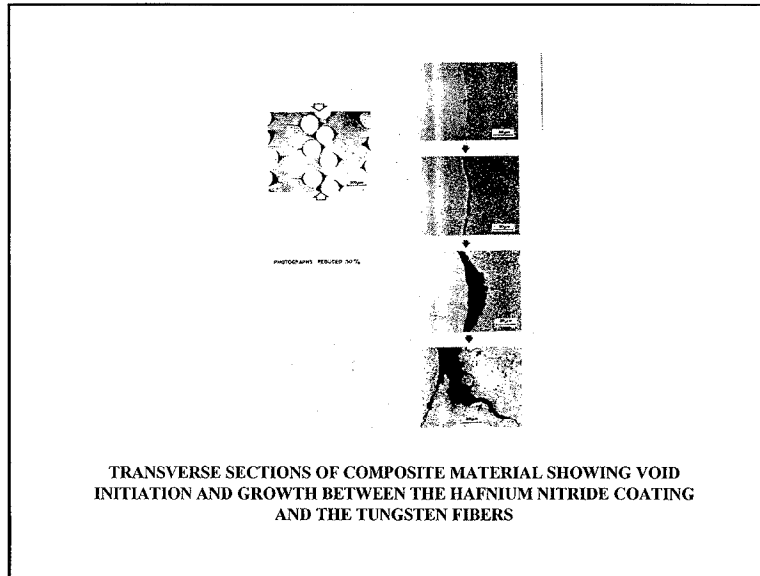
$10^{-3} \text{ s}^{-1}; 5X$

STRAIN=0.3
TEMP. = 1100°C



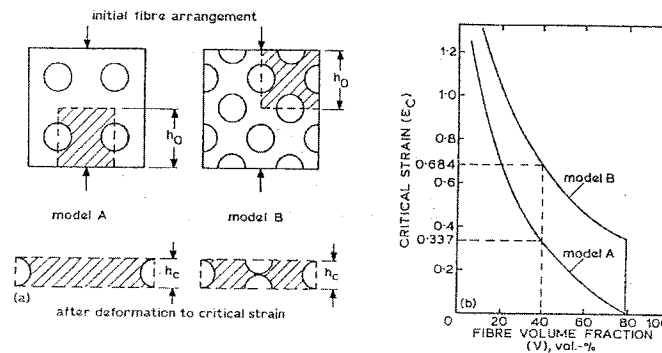
$10^{-4} \text{ s}^{-1}; 5X$

EFFECT OF STRAIN RATE ON HOT DUCTILITY OF COMPOSITE BLANK



FORMING LIMITS OF FRC

- METALLURGICAL NATURE: BASED ON NUCLEATION AND GROWTH OF MICROVOIDS
- GEOMETRIC NATURE: ACCOUNTS FOR FIBER CROSS-SECTION, STACKING ARRANGEMENT, VOLUME FRACTION



a models A and B for fibre packing arrangement; *b* effect of fibre packing arrangement and fibre volume fraction on critical strain for fibre damage

UPPER BOUND FORMING LIMIT IN METAL-MATRIX COMPOSITES

CONTROL OF VOID FORMATION

- SELECT FINE MESH POWDER
- IMPROVE BOND AT FIBER/MATRIX INTERFACE
- FORGE AT HIGH TEMPERATURES AND SLOW STRAIN RATE
- INCREASE ASPECT RATIO (W_0/H_0)
- ADD EXTRA MATRIX MATERIAL TO EXERT BACK PRESSURE ON COMPOSITE (CRITICAL AREAS)
- FORGE BELOW CRITICAL STRAIN

CONCLUSIONS

- FLOW STRESSES FOR THE COMPOSITES ARE ALWAYS SUBSTANTIALLY HIGHER THAN THOSE OBSERVED FOR THE NON-REINFORCED MATRIX MATERIAL FOR THE SAME FORGING CONDITIONS.
- FORMING LIMIT DIAGRAMS WERE DEVELOPED TO DEFINE REGIONS OF TEMPERATURE AND STRAIN RATE WHERE EARLY VOID FORMATION MAY BE AVOIDED
- DUCTILITY OF THE COMPOSITE MATERIAL IS GOVERNED BY THAT OF THE MATRIX. INCREASES AT HIGHER TEMPERATURES AND/OR SLOWER STRAIN RATE.

CONCLUSIONS (cont'd)

- FLOW STRESS OF THE COMPOSITE MATERIAL INCREASES SIGNIFICANTLY WITH ASPECT RATIO W_0/H_0 OF THE BLANK
- VOID FORMATION MAY BE REDUCED OR EVEN ELIMINATED BY INCREASING THE ASPECT RATIO W_0/H_0 OF THE COMPOSITE BILLET OR INCREASING FRICTION AT THE DIE/BILLET INTERFACE
- FORGING OF THE COMPOSITES NORMAL TO WIRE ALIGNMENT IS SHOWN TO RESULT IN PLANE STRAIN MODE OF DEFORMATION.

CONCLUSIONS (cont'd)

- FORMABILITY OF COMPOSITES IS LIMITED TO LOW STRAINS DUE TO THE FORMATION OF VOIDS AT THE TENSILE POLES OF THE FIBERS NORMAL TO THE LOADING DIRECTION. THE CRITICAL PARAMETER IN THIS CASE IS THE STRENGTH OF THE FIBER/MATRIX INTERFACE RELATIVE TO THAT OF THE MATRIX.
- TO ESCAPE VOID FORMATION AT THE EDGES OF THE BLANK, WHERE COMPRESSIVE STRESS IS LOW EXTRA MATRIX MATERIAL MAY BE ADDED TO EXERT BACK PRESSURE ON THE COMPOSITE IN THESE CRITICAL REGIONS. EXTRA MATERIALS CAN BE MACHINED OFF AFTER FORGING.

CONCLUSIONS (cont'd)

- A CRITICAL STRAIN EXISTS IN THE COMPOSITES AT WHICH THE FIBERS COME INTO CONTACT WITH EACH OTHER. BEYOND THE CRITICAL STRAIN, EXTENSIVE DAMAGE MAY OCCUR.
- THIS CRITICAL STRAIN IS A FUNCTION OF THE VOLUME FRACTION, STACKING ARRANGEMENT AND CROSS-SECTION OF THE FIBERS. IN THE PRESENT COMPOSITE MATERIAL, THE CRITICAL STRAIN WAS SHOWN TO BE 0.34 AND FORMING OF THE COMPOSITES SHOULD BE LIMITED TO STRAINS BELOW THIS VALUE.

INVOLVED COMPANIES AND RESEARCH CENTERS

- W-WIRES: GENERAL ELECTRIC (USA)
- FILAMENT COATING (HFN): WESTINGHOUSE CANADA
- POWDER TAPE: PRIVATE CO.
- COMPOSITE TAPE: WESTINGHOUSE CANADA
- HOT ISOSTATIC PRESSING: WESTINGHOUSE CANADA
- ISOTHERMAL FORGING: NRC

Behaviour of Expanded Metal During Tensile Loading Experiments and Modeling

A.M. Hashem¹, A. Kranz², M. Mahmoud² and E. El-Magd³

- 1 Prof. Dr., Production Eng. And Design Dept., Faculty of Engineering, Minia University,
61111 Minia, Egypt,
E-mai: fatah_hashem@yahoo.com
- 2 Research Assistant, and
- 3 Prof. Dr. Eng.
Lehr-und Forschungsgebiet Werkstoffkunde, RWTH Aachen, Augustinerbach 4-22,
D-52062 Aachen, Germany,
E-mail: elmagd@lfv.rwth-aachen.de

Abstract

The mechanical properties of the expanded metals behaviour is one of the important problems in the field of new cooling system in modern steam turbine which allows higher service temperatures and higher thermal efficiency. The effect of expanded metals geometry (i.e. two types of mesh, and different value of orientation angle) on the tensile behaviour has been investigated at room temperature. The two shapes of mesh were used, fine mesh (20 element/cm²) and coarse mesh (9 element/cm²). The influence of the orientation angle, changed from 0° to 180° in step of 15°, on the tensile behaviour was studied.

The experimental results show that the expanded metal is anisotropic materials depend on the loading directional. Tensile parameters such as yield load, load at 2% strain to fracture, ultimate load, stiffness and strain to fracture are determined for different orientation angle and two types of expanded metal. The finite element methods (FEM) has been used as a comparison study for the experimental results.

Keywords

Expanded metal, fine and coarse mesh, tensile behaviour, FEM, stiffness.

1. Introduction

Expanded metal is one of the most versatile products on the mechanical applications. The various types of expanded metal can be manufactured using the raw materials, including stainless steel, aluminum, carbon steel, titanium and copper. Expanded metal can be found virtually everywhere such as filters, grating, truck tool, fireplace, air condition, etc. and now using in the field of cooling system of the modern turbine.

The influence of the expanded metals and the orientation of the meshes on macroscopic mechanical behaviour is one of the important problems in the field of new cooling system in modern steam turbine to improve the thermal efficiency. The relationship between the orientation angles and the deformation on mechanical properties of materials, however, is not obvious. Furthermore, the distribution morphology of expanded metals in most engineering materials is irregular. Heat transfer and friction factor correlations for artificially roughened ducts with expanded metal mesh as roughness element was studied by Saini [1]. It has been that a considerable enhancement of heat transfer can be obtained as a result of providing expanded metal mesh artificial roughness on the absorber plate.

Takuda et.al [2] were applied the prediction of forming limit in bore expanding. Namely,

the bore-expanding process was simulated by the rigid-plastic finite element method combined with the ductile fracture criterion. The calculations were carried out for axisymmetric bore-expanding tests of various aluminum alloy sheets.

Over the years several aids to the design of perforated plates have been developed. The compilation of empirical design nomograms is standard way of providing design aids but other methods, combining experimental and theoretical investigations, have also been used in order to gain an understanding of the physical responses to any loads- applied singly or in combination [3-6].

Dilthey et.al [3] have been examined and characterized the behaviour of the porous structure under high-temperature loading. Tensile behaviour (of expanded metal and perforated sheets), shear-tensile and cross-tensile behaviour of welded structures were also investigated. Improving thermal efficiency in modern steam turbines can only be achieved by the application of new cooling system, such as effusion cooling. The materials properties of the structures were determined simultaneously, partially with redesigned testing methods.

El-Magd et.al [4] has been studied the anisotropic behaviour of perforated plates under tensile behaviour. The influence of the geometrical parameters on the tests are determined. Furthermore, an FEM computation is used to describe the experimental results. They concluded that the geometrical anisotropy of perforated plates independent of their material.

Others [5-7] have used FEM to analysis the performance assessment of perforated plates subject to general loading conditions. It should be emphasized that the mechanics of each mode of deformation of the plate was studied individually. The loading applied has been limited to elastic deformation which is as it should be in practice.

The objective of this experimental study is to investigate the effect of expanded metal mesh geometry (fine and coarse mesh) and / or the force plane angle on the tensile behaviour at room temperature. The recently proposed methods is applied to prediction of forming limit in expanded metals. The expanding process is simulated by Finite Element Method (FEM). The calculated results of the load-strain behaviour are compared with the experimental ones, and the validity of the present approach is discussed.

2. Experimental Work

The material used in this study is the mild steel St12 (AISI 1008, cold drawn). The chemical composition of this material is given in Table I. The mechanical properties of the AISI 1008 is given in Table II.

Table I Chemical composition of AISI 1008

Component	C	P	Mn	S	Fe
Wt. %	0.10	0.04	0.40	0.05	99.0

Table II Mechanical properties of AISI 1008

Ultimate tensile strength, MPa	Yield tensile strength, MPa	Elongation, %	Modulus of elasticity, GPa
340	285	20	205

The tensile test have been carried out at room temperature. The two types of mesh were used, fine mesh (20 element/cm²) and coarse mesh (9 element/cm²). The orientation of the test angle changed from 0° to 180° in step of 15°.

The dimension of the two shapes of mesh are shown in Table III. Fig. 1 shows the graphs of the mesh dimensions and orientation.

The tensile test were carried out in LFW/ RWTH Aachen, Germany by using MTS machine (capacity 25 kN). This machine was computerized and measured in whole test the load, elongation by two methods (extensometer and cross head displacement), time and calculated the stress and strain. Tested specimens were plates having 20 mm width and 100 mm length. The elongation was measured using a sensitive extensometer for the gauge length equal to 25 mm. In this way, strain and load were measured with a resolution of which allows an exact determination for the tensile behaviour. All specimens were tested till fracture occurs. The speed of the cross head was 3 mm/min for coarse mesh and 1 mm/min for fine mesh.

Table III Expanded metal dimensions

Symbol, mm	l	B	C	s	A
Coarse mesh	7.0	3.0	0.8	0.5	1.0
Fine mesh	4.0	2.5	0.5	0.2	1.0

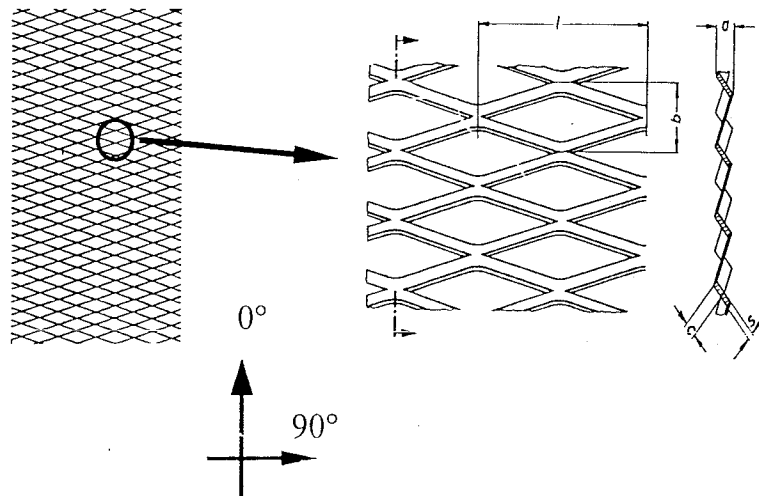


Figure 1 Geometrical definitions and reference-direction of expanded metal.

3. Experimental results

Tensile tests were carried out on two shapes, fine and coarse meshes, with different values of orientation angles from zero to 180 degree in step 15°. The load-strain curves is given in Fig. 2. The results obtained from a servohydraulic testing machine show significant differences for different orientation angle. The failure of each angle is clearly seen as a sudden decrease of the force in the tensile test. The comparison for the resulting load-strain curves show an increase of the load with increasing orientation angle. A load angle equal to 90° leads to the maximum value of load.

Table IV shows the experimental variation of the mesh at the beginning and at fracture for coarse meshes and different angles. From this table, it can be seen that the mesh elements are rotated around the tangent axis of the applied load.

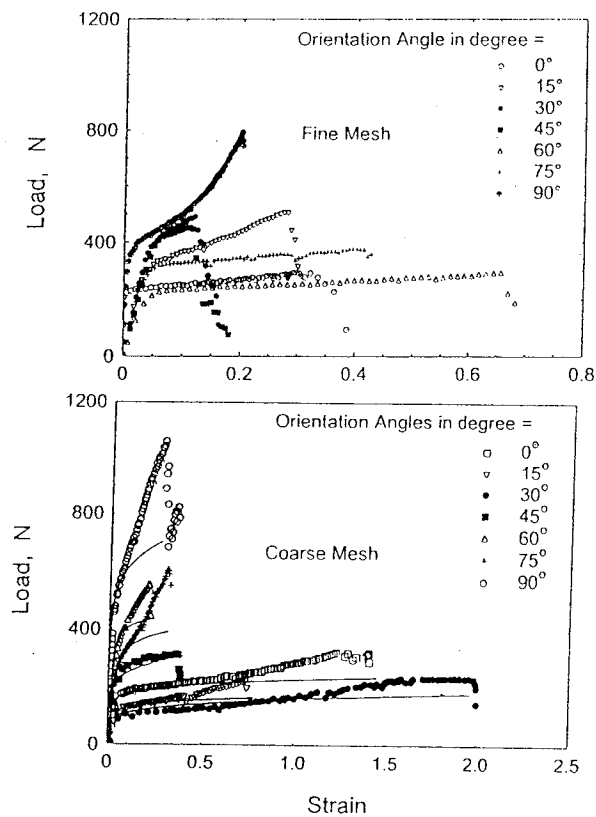


Figure 2 Load as a function strain for two meshes (fine and coarse mesh) and different orientation angle

Table IV Experimental variation of the meshes at the beginning and after fracture for coarse mesh and different orientation angle.

Orientation	0°	15°	30°	45°	60°	75°	90°
Before fracture							
After fracture							

4. Mechanical modelling

A coarse shape of mesh is chosen for the description of the tensile behaviour of expanded metal. Figure 3 shows the meshes used in 2D elastic-plastic finite element analysis of the deformation of an expanded metal for the angle equal to 0°. The deformation behaviour was calculated for whole specimens.

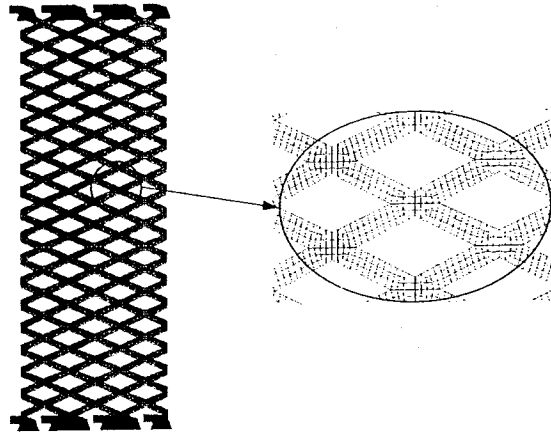


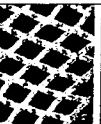
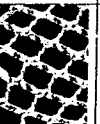
Figure 3 Unit model of expanded metal mesh used in FE analysis for angle 0° .

Finite element calculations are carried out in ABAQUS in order to describe the tensile behaviour. The model length is 55 mm and width is 20 mm (25 000 plane-stress elements) and the reaction forces and displacements of a cell around the mesh are determined. A load-strain curve is calculated using linear-elastic, linear-plastic model.

In the same figure (Fig. 2), the finite element data as a function between load and strain are given. The comparison between experimental results and FEM data are very closely in the elastic zone, while small difference in the plastic zone. In the orientation angle equal to 45° , the load strain curve is very closely in whole curves.

Table V shows the FEM variation of the mesh at the beginning and at fracture for coarse meshes and different angles. From this table, it can be also seen that the mesh elements are rotated around the tangent axis of the applied load.

Table V FEM variation of the meshes at the beginning and after fracture for coarse mesh and different orientation angle.

Orientation	0°	15°	30°	45°	60°	75°	90°
Before Fracture							
After Fracture							

5. Discussion

To analysis the loads on the fine and coarse meshes for expanded metal with an inclined angle orientation have been performed. Fig. 4 a&b show the relationship between yield load, load at 2% strain to fracture and ultimate load with different orientation angle for two shapes (fine and coarse meshes). From these figures, it is clear that the ultimate load increases with increase test angle till certain limit then start to decrease, and the highest value of the yield load and load at 2% strain to fracture and ultimate load at angle equal to 90° . Because of the anisotropic material structure, the load for different stages are strongly direction effected. Also, it is noticed that these relationship is very exactly symmetrical behavior around angle 90° .

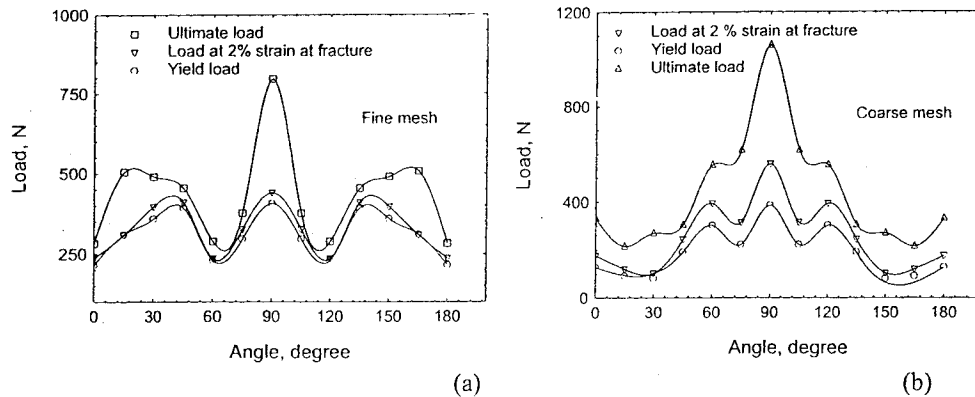


Figure 4 Load as a function of angle for two shape of meshes, fine and coarse mesh.

As expected, the highest value of ultimate load can be found for the orientation angle equal to 90° . In this case, the fracture mechanism takes two steps. In the first step, the mesh is moved in the direction perpendicular to the applied load, e.g. till yield load. In the second step, the resistance of the material to the load increase because friction between meshes (see Table IV and V) and the specimen becomes like solid specimen. Therefore, the 90° gives the maximum difference between results of the FEM result and the experimental data. In contrast, the yield load and load at 2% strain to fracture are evenly distributed around the orientation angle. Also, the decrease of the tensile behaviour in the 0° because this direction is the same direction of the metal forming to produce expanded metal, while in the direction perpendicular to metal forming gives the highest value of the tensile loading. Therefore, the fracture in this case at the beginning the mesh element return to the original shape and then the specimen like also solid specimen and the resistance to load is increased compared with other cases.

The relationship between strain to fracture as a function of angle is shown in Fig. 5 a&b respectively for two shapes of mesh. These figures indicate the decrease in ultimate load which means an increase in ductility. On the other hand, the highest value of the strain to fracture is found at 30° for the coarse mesh, while 60° for the fine mesh. Also, it is clear that the strain to fracture for the coarse mesh is lower than the fine mesh. The characteristic values of strain to fracture increase

with increasing angle which means that the deformation resistance will decrease by the increased angle of mesh.

Figure 5 a&b represent the relationship between stiffness (slop of load-elongation in elastic zone) and orientation angle for two shapes of mesh. From these figures it is clear that the maximum value of stiffness can be found at 90° for both shapes. Also, it is clear that the stiffness of fine mesh is higher than the coarse mesh.

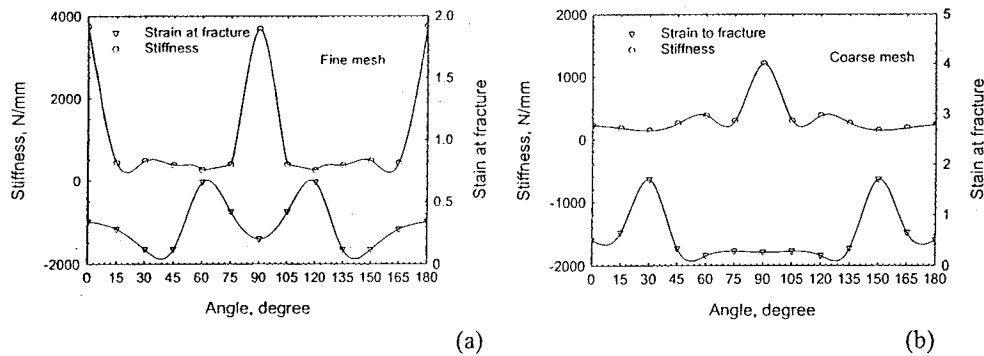


Figure 5 Stiffness and strain to fracture as a function of angle for two mesh types.

6. Comparison between experiments and FEM

The influence of the orientation angle for the coarse mesh was calculated by using FEM analysis. In order to compare the calculated values of the yield load, load at 2 % strain to fracture and ultimate load for different angles with the experimental results, shown in Fig. 6. It can be seen that the yield load and load at 2 % strain to fracture are mostly identical.

The predicted values of the ultimate load are show significant small differences with the experimental ones. The differences may be due to the friction between the meshes, therefore, at the force angle equal to 45°, the calculated and experimental data are very closed.

It has to be that for all of the orientation angle for comparison of FEM and experimental results, the load at yield, 2 % strain to fracture and ultimate become maximum in the angle equal to 90°, where the meshes are approximately tangent to the applied load direction. Due to the high value of ultimate load in tangential direction the maximum anisotropic material potential exists. But in a small variation in orientation angle from this optimum point, the ultimate load decreases in such a way, that the ultimate load reach to minimum value. This sensitivity of the strength characteristics requires a refined analysis of both load and strength for a load-adapted design of highly loaded expanded metal mesh.

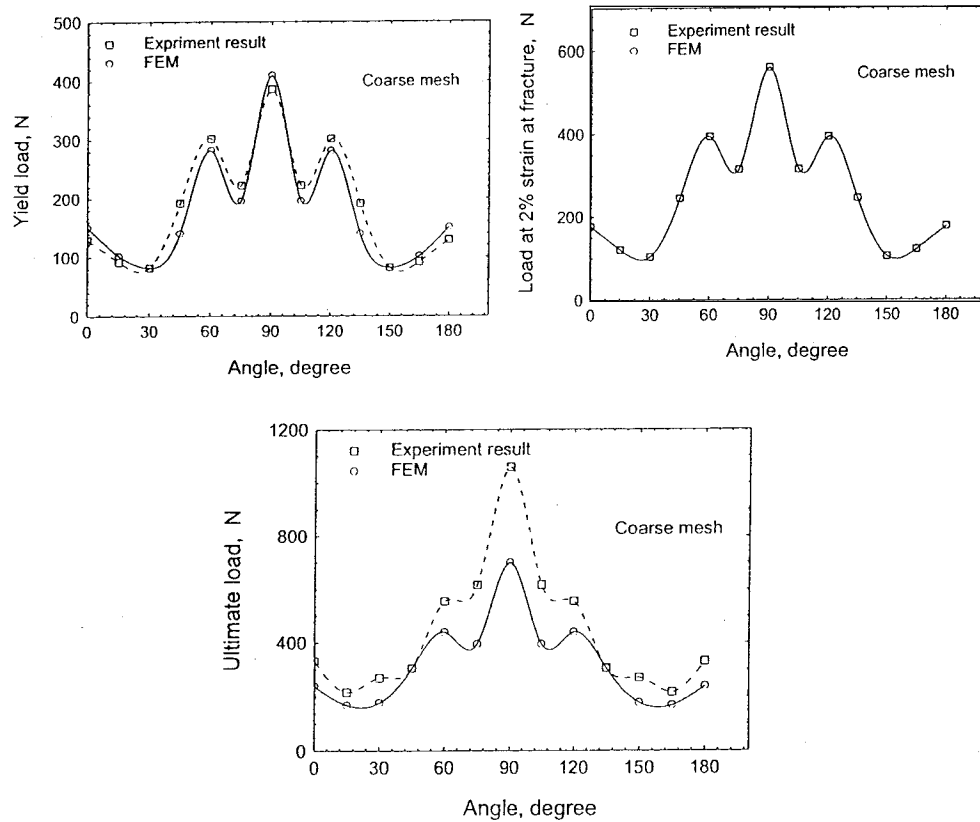


Figure 6 Comparison between experimental work and FEM results for the yield load and load at 2 % strain to fracture as a function of angle for coarse mesh .

7. Conclusions

The tensile behaviour of the mild steel AISI 1008, cold working was examined at different values of orientation angle of expanded metals with two different shapes of mesh: a fine and a coarse mesh.

1. The relation between ultimate tensile strength and flow stress at 2% strain for both shapes is very symmetrical around the 90°.
2. The highest value of the yield load, load at 2 % strain to fracture and ultimate load at the orientation angle equal to 90°. a small variation in orientation angle from this optimum point, the loads decreases in such a way.
3. The stiffness of the fine shape is higher than the coarse shape.
4. The rotation of the coarse mesh around the tangent axis of the applied load is higher than the fine mesh. Therefore, strain to fracture of the coarse mesh is higher than the fine mesh in the range of 15° to 60°.
5. The mathematical modeling by using finite element method (FEM) are mostly identical compared with the experimental work in the range of elastic zone (yield load and load at 2 % strain to fracture, while the ultimate load show significant difference. This may be attributed to the rotation of the meshes around to tangent load direction and the friction between meshes during the plastic zone.

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FRACTURE MECHANICS APPROACH to STRESS CORROSION CRACKING

Wolfgang Dietzel

GKSS-Forschungszentrum Geesthacht GmbH, Germany
and

Safwat Waheeb Sharkawy

Atomic Energy Authority, Egypt

Abstract: In this paper a general approach to the stress corrosion cracking (SCC) phenomenon and the underlying mechanism is briefly given. The main SCC test methods for smooth specimens and the linear elastic fracture mechanics (LEFM) approach with respect to testing of pre-cracked specimens are out-lined. The merits as well as the drawbacks of each method are discussed.

Key words: stress corrosion cracking, slow strain rate tests, constant load tests, rising displacement test, constant displacement test, stress intensity factor, strain rate, linear elastic fracture mechanics.

1.INTRODUCTION

Stress corrosion cracking (SCC) or, more general, environmentally assisted cracking (EAC) is the process which describes the failure of materials (pure metals, alloys, ceramics and polymers) in service due the synergistic effect of a corrosive environment and sustained tensile stresses. The corrosive environment can be a gas (as in case of zircaloy-iodine combination) or a liquid (as in case of steel-chloride solutions combinations). The values of the stresses required for the occurrence of SCC can be much less than the yield stress of the material. These stresses may be applied stresses, thermal stresses, or residual stresses (due to welding, cold deformation, heat treatment, prior loading or even build up of corrosion products). The direction of stresses influences the susceptibility of a material to SCC. Transverse stressing is considered more detrimental than longitudinal ones. SCC cracks may initiate at chemically inhomogeneous sites, pits created as a result of the surface being chemically attacked, or micro-cracks in the protective oxide film.

Linear elastic fracture mechanics (LEFM) is a well-established tool to study SCC, assuming that the plastic zone ahead the crack tip is of negligible size. In this case, the elastic stress intensity factor at the crack tip is considered as the mechanical driving force for both of crack initiation and propagation. Failure of a material due to SCC may occur either by slow crack growth or catastrophically. However, in either of these cases no

indications for failure may be noted before its occurrence. Materials which failed by SCC are often characterised by an only small reduction in the fracture area. This feature can be used as a measure when comparing the susceptibility of different materials to SCC.

The fracture mode of materials which failed by SCC is usually described as brittle failure. When cracks follow the grain boundaries they lead to intergranular stress corrosion cracking (IGSCC). In this case, the grain boundaries are anodic with respect to the grains and are hence more susceptible to corrosion. This effect can be due to precipitates, depletion, adsorption, or enrichment of elements. Generally, the cracks are branched and propagate in a direction nearly perpendicular to that of stress. However, in some cases non-branched cracks are observed along branched ones. Cracking through specific crystallographic planes within the grains leads to transgranular stress corrosion cracking (TGSCC), which is characterised by cleavage and river patterns. Both of these cracking types can occur on the same fracture surface of a material which failed by SCC. The cracking type can in some materials be changed by altering the materials' metallurgical conditions, while in others this change can be achieved by altering the environmental conditions.

It is worth to mention that SCC is a time dependent phenomenon and is controlled by material composition, microstructure as well as the electrochemical conditions at the crack tip. The electrochemical conditions include temperature, potential, pH and concentration of species inside the crack.

The SCC problem deserves great concern as it is considered a serious corrosion problem causing loss of lives (as in case of failure of boilers, aeroplanes, bridges etc.) and affecting the international economy (as in case of failure of petro-chemical plants or off-shore platforms). Despite the tedious efforts which were made in the last decade to find a general analytical approach that can predict which combinations of a material and an environment result in SCC, yet it is not available. Therefore, at the present time all guidance for avoiding SCC during service has to be based either on past experience or on laboratory tests.

2. SCC-MECHANISM

The active path and the stress-sorption are the most widely accepted SCC-mechanisms. These two mechanisms can to a large extent explain the SCC mechanism. Nevertheless, no single mechanism is capable to answer the many questions regarding this phenomenon.

2.1 The Anodic Dissolution (Active Path Dissolution, APD)

In this mechanism crack nucleation occurs through some steps. Namely, passivation (denoted by P in Fig.1) of the tested specimen surface, localised attack (denoted by A in Fig.1) and penetration of the passive film where micro-notches are created. The dissolution and transport rates at the crack tip must be higher than those at its sides in order to be retained (Fig.1). The sustained tensile stresses brake the re-passivated film at the crack tip even if it is formed. The crack sides are in a passive state while the crack tip is in an active one. Anodic segregated elements are considered as active sites for crack

initiation and further active path dissolution by establishing a galvanic cell. This mechanism is, usually, typical for low and medium strength materials.

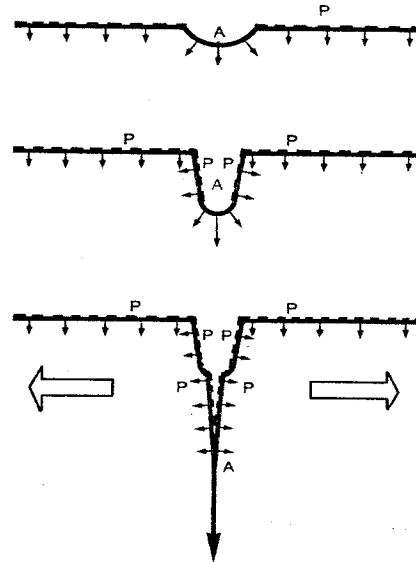


Fig. 1 - Illustration of the active path dissolution (APD) mechanism.

2.2 The Stress Sorption Mechanism

In this mechanism SCC occurs as a result of a weakening of the cohesive bonds of surface-metal atoms by adsorption of damaging species in the corrosive environment. This is accompanied by a reduction of the surface energy (stacking fault energy decrease) of the material which supports cracking under the applied tensile stresses.

3. SCC TESTING of SMOOTH SPECIMENS

3.1. Constant Load Test

In this classical test a smooth tensile specimen is placed in the corrosive environment and is stressed by a tensile dead load. The stress of the tested specimen is simply calculated by dividing the applied load by the specimen's cross-section area. In case of testing tubular specimens an internal constant pressure replaces the tensile dead load. In this case the hoop stress, σ_h , is calculated as:

$$\begin{aligned}\sigma_h &= PD (1 + \epsilon_p) / 2t (1 - \epsilon_p) \\ &\cong PD (1 + 2 \epsilon_p + \dots) / 2t\end{aligned}$$

where:

P is the applied pressure

ϵ_p is the plastic circumferential strain after applying the pressure

D is the tube's average diameter
 t is the tube's thickness

From a constant load test the time-to-failure, t_f , failure stress, σ_f , elongation to failure, ϵ_f , reduction in area, threshold stress, σ_{th} , the average crack propagation rate, $(da/dt)_{SCC}$, and the fracture mode can be determined. The more tests are carried out at stresses close to that predicted threshold stress, the more accurate the value of this stress will be (Fig.2). The value of the threshold stress varies from one material-environment combination to another. However, it is in the range of $\sim 10 - 70$ % of the yield stress of the material. Some investigators claim that there is no actual threshold stress for a specific material-environment combination, as it depends on how patient the investigator is, i.e. on the duration of an individual test.

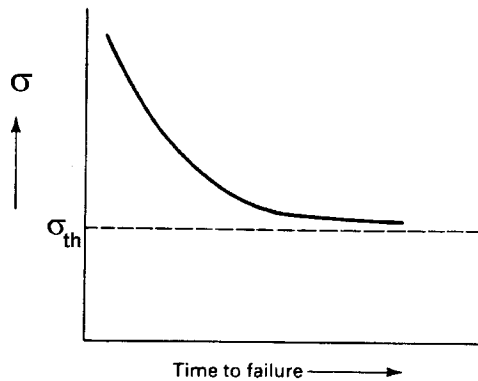


Fig. 2 - The failure stress-time to failure relation for a material tested by the constant load method.

This method has the disadvantage of long experimental time during which many factors may change. However, its simplicity and the use of inexpensive equipment are acknowledged.

3.2. Slow Strain Rate Test

The slow strain rate test (SSRT) is also known as a constant extension rate test (CERT). In this test the smooth specimens used are similar to that of mechanical tensile testing. The specimen under test is placed in the corrosive environment, the load is applied and the specimen is strained at a controlled constant rate. Usually, the applied strain rate is in the range of 10^{-5} to 10^{-8} s^{-1} . High strain rates lead to mechanical rupture as the electrochemical processes have not the enough time, while very slow strain rates can result in passivation. Every material-environment combination which is susceptible to SCC has a range of strain rates in which it shows high susceptibility to environmental cracking (Fig.3). In some materials with low susceptibility to SCC, strain rates as low as 10^{-12} s^{-1} may be required. However, it should be noted that the local strain rate (effective strain rate) measured at the gauge length of the specimen is considered as an important

parameter in the SCC process rather than the nominal one determined from the cross-head speed of the test machine.

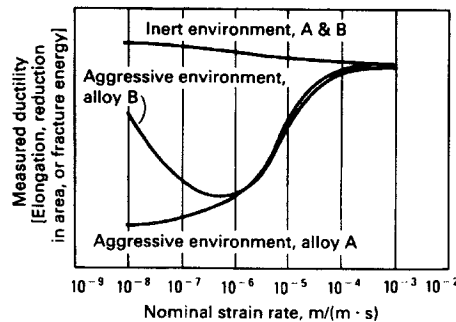


Fig. 3 - The measured ductility-nominal strain rate relation for two alloys (A, B) tested by the SSRT method in an aggressive environment (test results in an inert environment are plotted for comparison).

The SSRT enables the knowledge of the time to failure of the material under the studied conditions as well as the failure stress, reduction in area, elongation to failure and fracture mode. The average crack growth rate is simply calculated by dividing the SCC depth (observed by the SEM) by the time to failure, t_f , without accounting for the crack incubation time although in a flaw-free and homogeneous material it can be significantly longer than the time for crack propagation. Some investigators claim that 90% of the time to failure is spent for the crack initiation (incubation) process. However, the thus determined average value of the crack growth rate is widely accepted as a reasonable measure to estimate how fast an SCC crack can grow into the material. Taking a factor of safety for such crack growth or subtracting an estimated incubation time may be helpful to get better prediction of the lifetime of a component in service. Comparing the obtained results in the corrosive environment with those for the material tested in an inert environment (usually air or, in some cases, argon) is beneficial to determine the susceptibility of materials to SCC. Tests can be carried out either at open circuit potential or with the specimen being polarised to the required potential with respect to the corrosion potential of the material in the corrosive environment of interest.

The SSRT method has some merits, as it is a dynamic technique leading to failure of the tested specimens in a reasonable time of at most few weeks (depending on the strain rate used). It also, minimises the crack initiation time due to breaking of the surface oxides. The disadvantage of this technique is the use of expensive and sophisticated equipment.

4. FRACURE MECHANICHS APPROACH to SCC

The fracture mechanics assessment of the materials susceptibility to SCC is usually based on linear elastic fracture mechanics (LEFM). In this approach, the elastic stress intensity factor for the opening mode (Mode I), K_I is used to characterise the mechanical driving force for the initiation and propagation of cracks.

According to LEFM, the stress, σ_{yy} , at a distance, r , from a crack tip is calculated as:

$$\begin{aligned}\sigma_{yy} &= \frac{K_I}{\sqrt{2\pi r}} \\ &= b\sigma \frac{\sqrt{a}}{\sqrt{2\pi r}}\end{aligned}$$

where σ is the uniform tensile stress applied to a plate. Since the stress depends on the crack size, a , the value of σ_{yy} is therefore equal to

$$\sigma_{yy} = B\sigma \frac{\sqrt{\pi a}}{\sqrt{2\pi r}}$$

And as the crack tip stress will be higher when W (the width of a plate subjected to uniform tension) is small; B will be a function of (a/W) and the value of K_I will be

$$K_I = \sigma \sqrt{\pi a} f\left(\frac{a}{W}\right).$$

Fracture occurs when the value of K_I exceeds a critical value denoted by the fracture toughness of the material, K_{IC} .

It should be noted that LEFM approach to SCC is based on the assumption that a limited amount of plastic deformation is existing ahead the crack tips. This is not justified in low-strength alloys with high SCC resistance or in creep cracking. In this case, the elastic-plastic fracture mechanics (EPFM) should be applied. The J-integral or crack tip opening displacement (CTOD) is then used as the mechanical crack driving force.

4.1. The da/dt-K Relation

The accumulated SCC results for pre-cracked specimen/environment combinations indicate that there is a characteristic relation between the logarithm of the crack propagation rate (da/dt) and the elastic stress intensity factor, K_I , as illustrated in Fig. 4. The lower shelf of this curve gives the threshold value of K_I , namely K_{ISCC} . Below this value, SCC can hardly occur or crack propagation rates are very small.

In region I the crack propagation is strongly dependent on K_I . In the plateau region (Region II), the propagation rate is independent on K_I . In this region (which in many material-environment combinations may be absent) transport and electrochemical processes control the crack propagation kinetics.

In region III, the propagation rate is again strongly dependent on K_I . When the K_I value reaches the fracture toughness of the material for plane strain, K_{IC} , the material fails by mechanical rupture. Therefore, the knowledge of this da/dt - K relation is beneficial in determining the rate of propagation of already existing cracks subjected to the specific load and exposed to the corrosive environment.

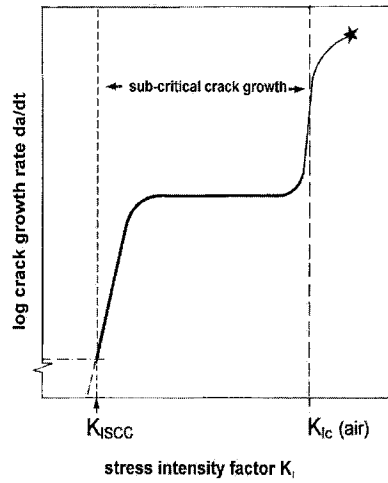


Fig. 4 - The stress intensity factor (K_I)-crack propagation rate (da/dt) relation.

4. 2. Influence of σ_y on K_{ISCC}

The use of the parameter K_{ISCC} thus determined is illustrated in Fig. 5. In this figure data of K_{ISCC} are plotted versus the yield stress, σ_y , for various high strength steels in salt water. In this so-called Ratio Analysis Diagram (RAD) the straight lines represent the maximum allowable flaw size of a material when it is subjected to a stress equal to its yield stress while being exposed to salt water.

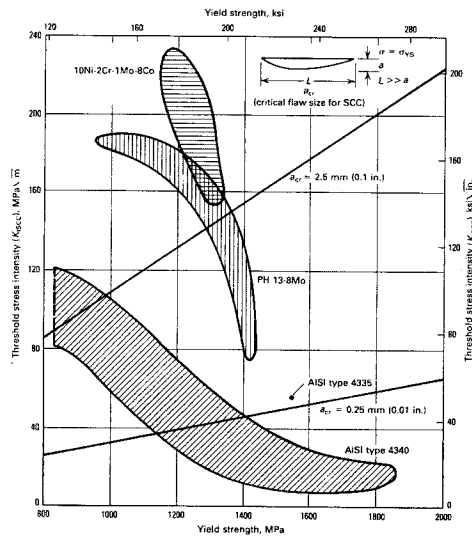


Fig. 5 - The Ratio Analysis Diagram (Sandoz, 1972).

5. FRACTURE MECHANICS BASED SCC TEST METHODS

Fracture mechanics techniques have been recently applied on pre-cracked specimens for SCC tests. This techniques have the merit of eliminating the error concerned with the incubation time of cracks as they are already existing, as well as calculating the elastic stress intensity factor, K_{ISCC} , for the tested material in that specific environment.

5.1.Constant Load and Constant Displacement Tests

Most fracture mechanics based SCC tests favour static loading techniques such as the constant load and constant displacement test (Fig. 6). In these test pre-cracked compact tension, C(T), and Double Cantilever Beam, DCB, specimens are used, respectively.

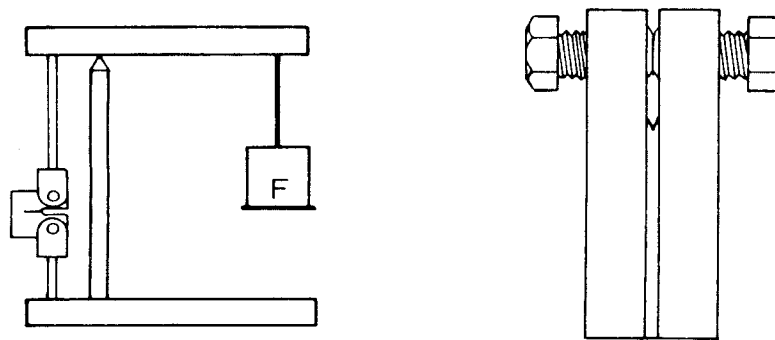


Fig. 6 - An illustration for:

- the constant load test on pre-cracked C(T) specimens (left),
- the constant deflection test on DCB specimens (right).

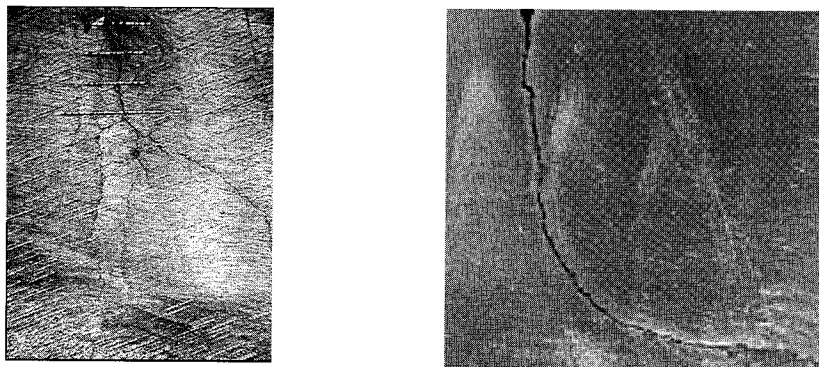


Fig. 7 - Crack branching (left) and crack growth off plane (right) in DCB specimens tested for SCC (steel AISI 316H in 100 ppm Cl solution, 90°C).

These tests are easy to carry out and require minimum laboratory equipment (Fig. 6). Despite the simplicity of these tests, a time as long as one year or more is required to determine the threshold values. Crack branching and off plane growth represent another disadvantage to these tests (Fig. 7).

5.2. Rising Displacement Tests

In-order to overcome the disadvantage of long test duration of the static tests, the rising displacement technique was adopted as a dynamic test method. In this test compact tension, C(T), specimens containing a sharp fatigue pre-crack are used (Fig. 8).

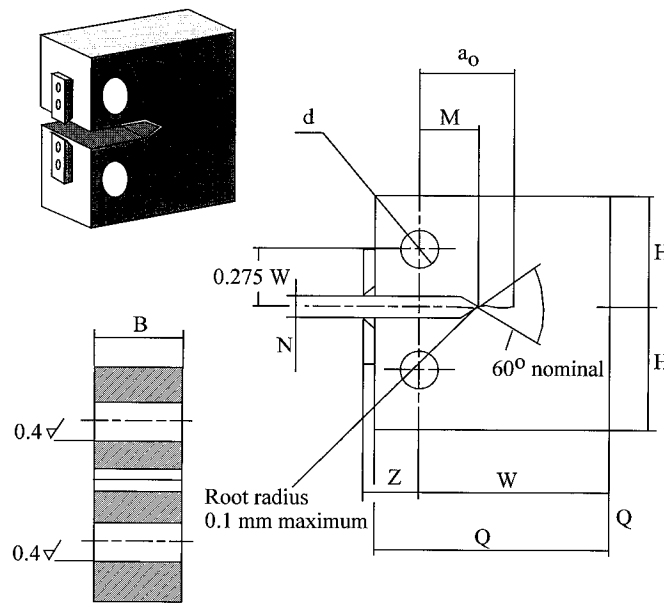


Fig. 8 - Proportional dimensions of the C(T) specimens used in rising displacement tests.

The specimens should fulfil the following requirements:

$$a, B, (W-a) \geq 2.5 \left(\frac{K_I}{R_{p0.2}} \right)^2 \quad \text{and} \quad \frac{a}{W} \leq 0.6$$

where:

- W is the specimen width
- a is the crack overall length
- B is the specimen thickness
- K_I is the material toughness
- $R_{p0.2}$ is the yield strength of the material.

Typically, the specimen is placed in the corrosive environment for 24 hours prior to testing and is kept under a low pre-load of ~ 0.5 kN to facilitate the entrance of the solution into the crack tip. Tests are usually run in a screw driven tensile machine which is controlled to give the required displacement rate for the C(T) specimen. During testing the load, P , the line displacement, v_{LL} , and the crack length are monitored. The DC potential drop, DCPD, technique is widely used to measure the crack length, a . In the version used here, a pulsed DC current is passed through the specimen at regular intervals during measurements only and its polarity is reversed while measuring. To detect the onset of cracking, the point at which a significant change in the DCPD signal occurs is identified from the load vs. DCPD plot or from the DCPD vs. v_{LL} plot. The K value corresponding to this load/displacement is considered the value of the stress intensity at crack initiation. The value of K_I is determined from :

$$K_I = \frac{P}{B\sqrt{W}} \frac{(2+a/W)}{(1-a/W)^{1.5}} [0.866 + 4.64a/W - 13.32(a/W)^2 + 14.72(a/W)^3 - 5.6(a/W)^4]$$

where:

- P is the applied load
- a is the crack length
- B is the specimen thickness
- K_I is the material fracture toughness.

This method has the merit of short testing time (as testing is carried-out under dynamic strain). Usually, neither crack- branching nor off plane growth occur in these tests. However, The disadvantage of this technique is the use of expensive and sophisticated equipment. Another drawback for this technique is the dependency of K_{ISCC} on the applied strain rate (see Fig .9).

5. 3. Comparison of SCC Test Results using Constant Displacement and Rising Displacement Techniques

In order to rely on a certain SCC testing technique, it should give reliable and reproducible results. This means that the results should be related to the material and environment but not to the test method. This was proven in tests which were performed on the high strength aluminium alloy Al 2024 T351 in the S-L orientation tested in 3.5% NaCl solution. In Fig. 9 results of tests are shown which were performed on pre-cracked compact tension, C(T), and double cantilever beam, DCB, specimens. Reference tests were performed in air. The C(T) specimens were tested at constant displacement rates between 10^{-12} and 3×10^{-8} m/s; the DCB specimens were tested under constant displacement. The values obtained for the threshold stress intensity factor, K_{init} , are plotted in this figure versus the displacement rate of the C(T) specimens.

It is clear from Fig. 9 that at the upper shelf region (high displacement rates) the stress intensity factor measured at crack initiation is - as should be expected - equal to the material's fracture toughness. This value of K_{init} decreases when decreasing the displacement rate, as a relatively longer time is allowed for the electrochemical and

transport processes to take place. A minimum threshold value has been predicted from this plot as $K_{ISCC} \cong 5 \text{ MPa}\sqrt{\text{m}}$, determined at a displacement rate of $\sim 10^{-10} \text{ m/s}$ with a test duration of about one month. This value perfectly matches the threshold value determined from long term testing (test duration $> 1 \text{ year}$) at the DCB specimens. Higher K_{init} values measured at even lower rates (10^{-12}) should not be surprising as repassivation and the formation of a thin oxide film processes may occur.

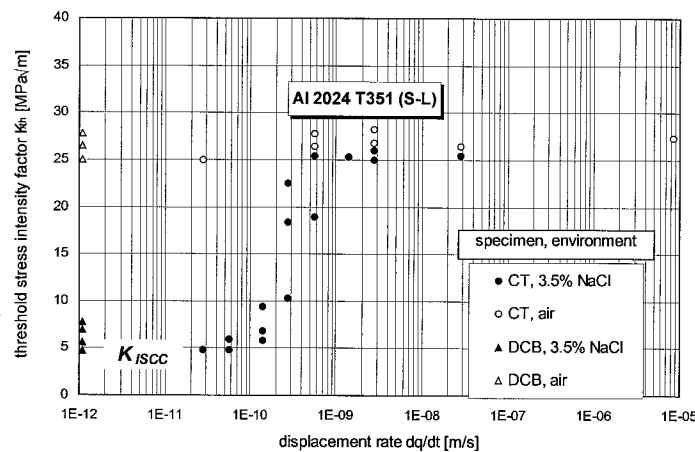


Fig. 9 - Influence of the displacement rate, dq/dt , on the stress intensity factor at crack initiation, K_{th} , measured in rising displacement tests on C(T) specimens and in constant displacement tests on DCB specimens.

6. CONCLUSIONS

- SCC is a time dependent phenomenon, controlled by microstructural and metallurgical features and by localised electrochemical processes at the crack tip.
- A generalised analytical approach based on micromechanics and physical metallurgy that would allow to predict which combinations of a material-environment results in SCC is not available, so far.
- Fracture mechanics approach to SCC is useful to evaluate the susceptibility of different materials to cracking in a reasonable time. This can help to get better understanding for the SCC phenomenon and mitigate this problem by developing new alloys having higher SCC resistance.
- Reliable results from the application of the fracture mechanics technique on SCC tests call for standardisation of these tests.

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Case Study
The Failure Analysis of Boiler Superheater Tubes
at Shoubra El Khema Power Station

Dr. Ahmed Gorab. Chem. Mohamad Abdel Rashed
and Eng. Seham El Zahany

Abstract:

The failed tube is elbow shape made of stainless steel (SA 213 Tp. 304H) subjected to loss of materials, severe corrosion, layer of outer scales, cracks and microcracks. The design temperature and pressure are 587 °C, 207 Kg/cm². Physical, chemical and metallographic inspection are carried out as follows:

- Chemical analysis of tube alloy and scale deposit measured by Energy Dispersive X-ray Analysis (EDX) attached to the scanning electron microscope.
- Measuring of Vicker's hardness number at different points of failed tube and a new one.
- Metallographic examination of failed tube and a new tube.
- Collection of chemical analysis data of boiler steam during one year.
- Collection of combustion analysis data and fuel oil analysis during one year.
- It was concluded that the failure of tube is referred to occurrence of sensitization phenomenon with appearance of intergranular corrosion of austenitic stainless steels which caused from the accumulation of chromium carbides at the grain boundaries and create stresses at them. The alloy becomes brittle and can not resist the designed inner pressure, which causes the failure. The sensitization phenomenon affects the austenitic stainless steels when heated in the temperature range of about 550 °C-850°C.
- It was recommended to replace all 3rd super heater tubes by another alloy with low carbon content 0.03 % or alloy contains additional elements such as titanium and columbium to be more tolerance to heat. Fuel oil treatment by chemical additives, combustion adjustment, and operation instruction during operation and outages should be followed and property controlled.

Egyptian Electricity Transmission Company
CENTRAL CHEMICAL LABORATORY

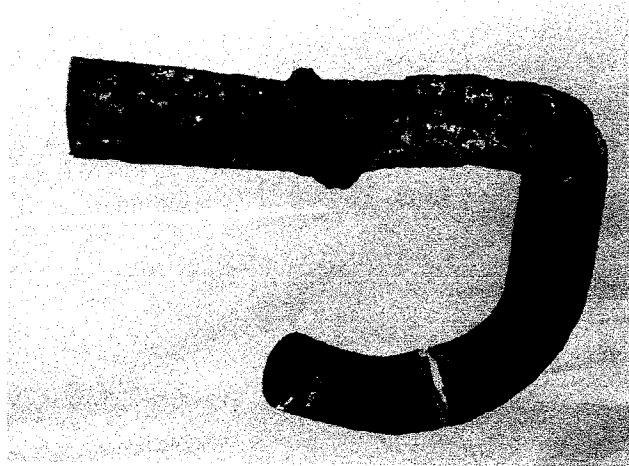
Central Chemical Laboratory help in solving all chemical problems of the power and transformer station and consists of many laboratories such as :

01. Water analysis lab.
02. Scale analysis laboratory.
03. Turbine and Transformer oil analysis lab.
04. Fuel analysis lab. For (liquid, solid and gas).
05. X-ray diffraction lab. Analysis lab.
06. Atomic absorption analysis lab.
07. Corrosion studies analysis lab.
08. Metallurgical studies analysis lab.
09. Water treatment studies lab.
10. Environmental measuring lab.
11. Scanning electron microscope & EDX lab.

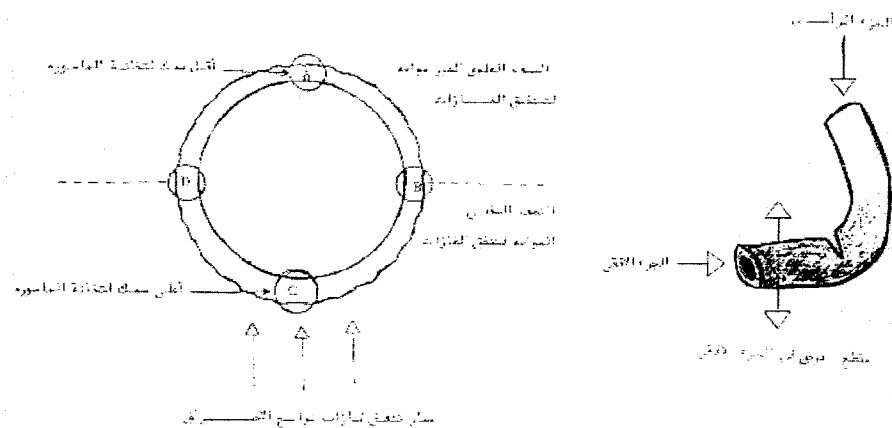
**CASE STUDY
FOR THE FAILURE ANALYSIS
OF BOILER SUPERHEATER TUBES
AT SHOUBRA EL KHEMA POWER STATION**

Sample Data:

- Type of the alloy: (SA213TP.304H) St. St. 304
C % = 0.1-0.4, Cr % = 18-20, Ni % = 8-11
- Temperature of steam flowed inside the tubes: 540 °C
- Temperature of flow gases outside the tubes: 1100 °C
- Fuel used: Mazout & Natural gas
- Initial operation: Oct. 1985
- Failure date: 1998
- Original thickness: 8.5 mm
- Design temperature: 587 °C
- Design pressure: 207 Kg/cm²
- Thickness of protective layer presence at the inner surface: 165 micron
- Vicker Hardness No. for a new tube: 182 V.H.N.
- Vicker Hardness No. for inner surface of failed tube: 245 V.H.N.
- Vicker Hardness No. for outer surface of failed tube: 330 V.H.N. - 390 V.H.N.

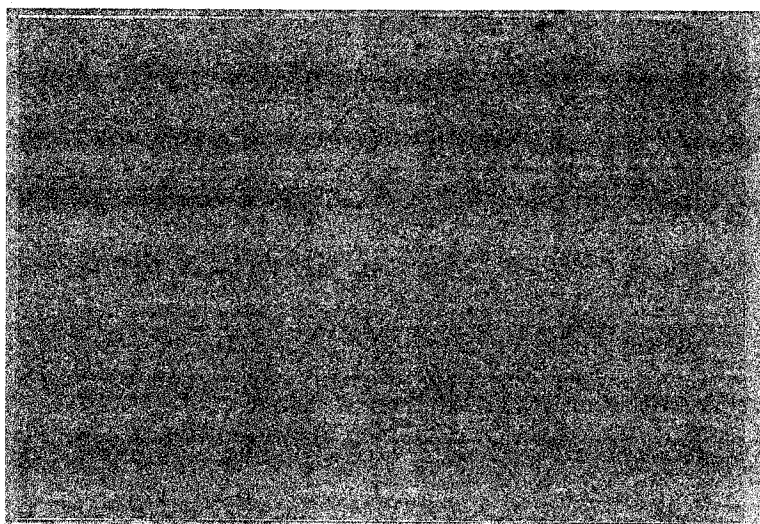


Optical micrograph for general view of the failed tube



**The measured thickness, hardness and
examined microscope sides
Positions (A, B, C and D)**

Grain Structure of the New Tube



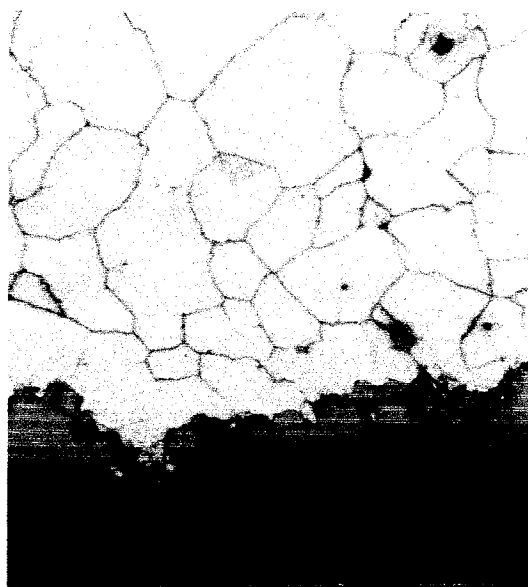
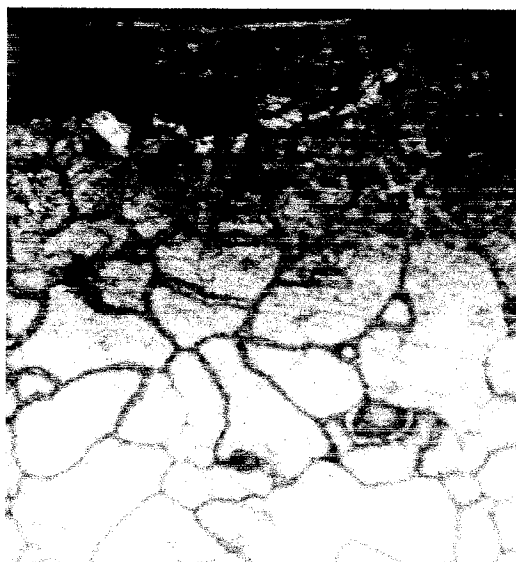
Magnification: 200X

Austenitic Stainless Steel

Upper side of the tube (Position A)

Magnification: 200X

Outer Surface

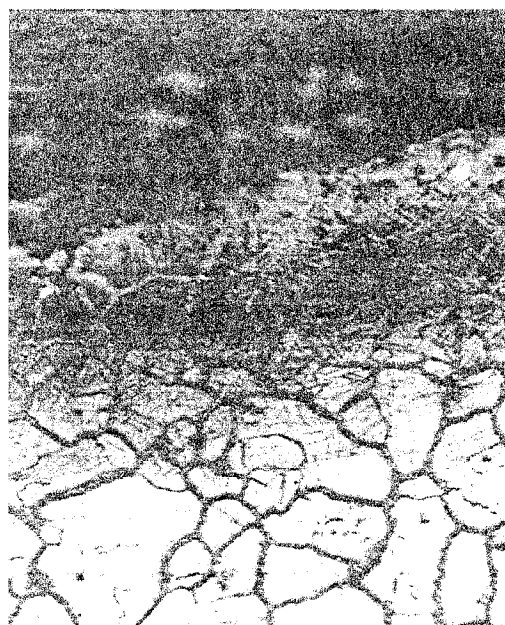


Magnification: 200X
Inner Surface

Right Side (Position B)

Magnification: 200X

Outer Surface



Magnification: 200X

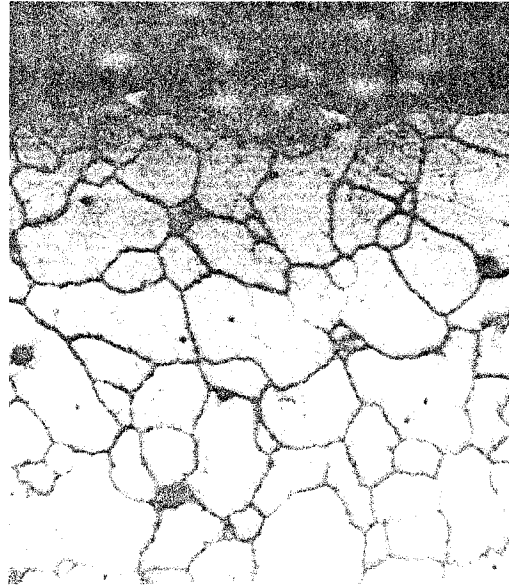
Inner Surface



**Lower side of the tube, which faced the combustion flue gases
(Position C)**

Magnification: 200X

Outer Surface



Magnification: 200X

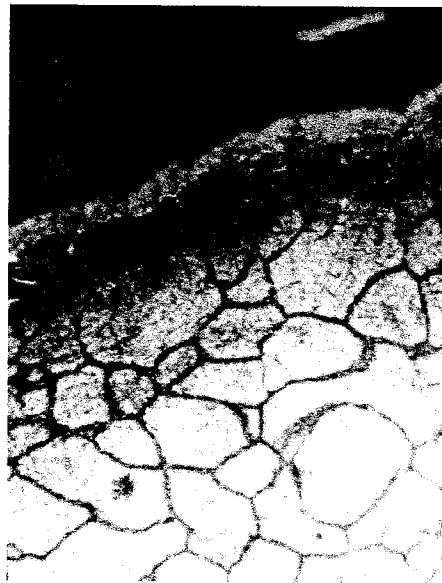
Inner Surface



Left Side (Position D)

Magnification: 200X

Outer Surface

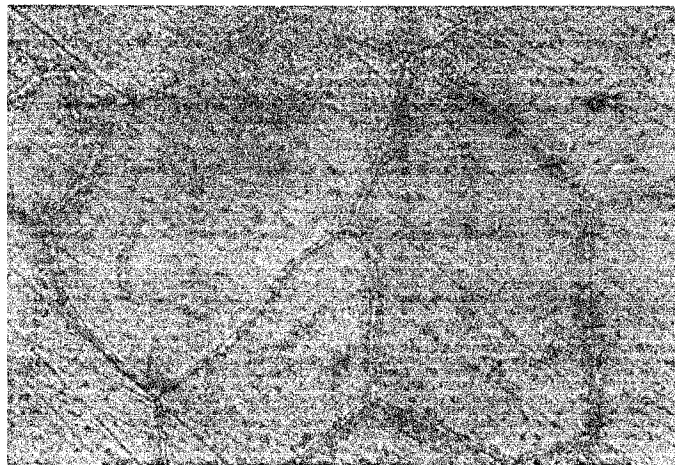


Magnification: 200X

Inner Surface



Magnification: 1500X



Magnification: 1000X

SEM micrographs
Shows precipitation of chromium Carbide of grain
boundary, which defined as Sensitization phenomena

SENSITIZATION

- It is a type of intergranular corrosion which occurred at austenitic stainless steel.
- Intergranular corrosion is preferential dissolution of the grain-boundary phases or the zones immediately adjacent to them because grain boundary zone is more active chemically than grain itself.
- Austenetic stainless steel become sensitized or susceptible to intergranular corrosion when heated in the temperature range of about 550 °C to 850 °C.
- At this range of temperature chromium depleted from the grain boundary and areas adjacent to it to combined with carbon and precipitated on grain boundary.
- The extent of sensitization effect is a function of both time and temperature also the composition of the alloy “specially the percentage of carbon and of carbide forming elements” also, sensitizing is damaging in a given instance depends on the requirements of the specific application and the environment and stresses to which it is exposed , the prior thermal and mechanical working history of the alloy.

The Remedy:

- One method of reducing the susceptibility of austenitic stainless steel to intergranular corrosion is to use solution heat treatment, usually by heating to 1066 °C to 1121 °C and immediately water quenching. By this procedure chromium carbide is dissolved and retained in solid solution provided that cooling of the steel from the solution.
- We can avoid sensitization by using stainless steels that contain less than 0.03 % Carbon (extra-low carbon grades), or by using stainless steels grades which contain sufficient titanium and columbium or columbium plus tantalum as stabilizing elements.

MICROSTRUCTURAL INSTABILITY OF THE WELDED JOINT OF P91 STEEL DURING CREEP AT 600 °C

M.E. Abd El-Azim*, G. Zies** and A. Klenk**

* Metallurgy Department, Atomic Energy Authority, Cairo, Egypt.

** Staatliche Materialprüfungstalt, Universität Stuttgart, Germany.

ABSTRACT

The martensitic 10 CrMoVNb 91 (P91) steel has been developed for the application of the highly ultra supercritical pressure for steam power plants. The creep rupture strength of the welded joint of this steel is limited by that of the fine-grained region of its heat affected zone (HAZ). The microstructural changes occurring in this region during long term creep test at 600 °C and 70 MPa were examined by optical microscopy and by scanning and transmission electron microscopy in comparison with the microstructure of this region after post weld heat treatment. The factors which result in the reduction of the creep rupture strength of the fine-grained region of HAZ were discussed. It was found that the most effective factor reducing the creep rupture strength of the fine-grained region of HAZ of the welded joint of P91 steel, in comparison with the coarse-grained region of HAZ and the base metal of the welded joint are the finer prior austenite grain size of the fine-grained region which accelerates the rate of growth of martensite lath subgrains and enhances creep cavitation and the lower peak temperature during welding which results in a softer martensite matrix.

INTRODUCTION

Martensitic heat resistant steels of 9-12 % Cr are candidate alloys for the main steam pipes, headers, boilers and other components in fossil power generation plants because they have the advantages of low thermal expansion, high thermal conductivity, good steam corrosion resistance and excellent creep resistance [1,2]. These advantages allow the steam power plants to operate at a high steam temperature more than 600 °C and a steam pressure greater than 300 bar [1].

The martensitic structure of these steels includes considerable amounts of dislocations in lath structure introduced by quenching after austenitizing so it has a good creep resistance [1]. However, in the case of welded joints, the fine grained region of the heat affected zone has lower creep rupture strength than the base metal [1,3] and so deteriorates the creep rupture strength of the welded joints.

The correlation between the creep properties and microstructures of 9Cr-1Mo-NbV and 9Cr-1Mo-NbVW steels have been studied extensively [4-10]; by contrast there are a few investigations on the microstructural evolution during creep for their welded joints [1,2,11,12]. The aim of this work is to study the role of microstructural instability of fine-grained region of HAZ on the creep behaviour of the welded joint of X10CrMoVNb 91 (P91) steel at 600 °C.

EXPERIMENTAL

Material and Heat Treatment

The material used in this study was P91 steel and was received as a tube of wall thickness of 85 mm and of outer diameter of 492 mm. Table 1 gives the chemical composition of this steel. This steel was austenitized at 1050 °C for 10 min and air cooled, then tempered at 760 °C for 2 h and finally air cooled. The welded joints were made by manual arc welding (MAW) of pipes and given a post weld heat treatment (PWHT) at 760 °C for 2 h, followed by air cooling.

For better comparison between this steel (base metal) and its welded joint, the same tempering treatment mentioned above (760 °C for 2 h) followed by air cooling was applied additionally to this steel. Some specimens of this steel were heat treated to get a microstructure similar to that of the fine-grained region of the heat affected zone of the welded joint. The heat input during welding was simulated by inductive overheating (heating time ~ 20 s from 22-850 °C) of the specimens to a peak temperature of 850 °C; then the specimens were held there for 3 sec and finally quenched in oil.

Creep Test

Creep tests were performed on the base metal, the welded joint and the specimens simulated to the fine-grained region of HAZ. The tests were carried out at 600 °C, in air and at various constant applied loads by using single and multi specimens, lever type creep machines. Cylindrical test specimens with a 36x12 mm uniform gauge cross section were machined from the base metal and from the specimens simulated to the fine grained region of HAZ and with a 70x12 mm uniform gauge cross section were machined from the welded joints. The test specimens of the welded joints were cross weld specimens where the centre of the weld metal of the welded joint was the centre of the uniform gauge length.

Examination Techniques

The welded joint specimens after PWHT, creep rupture test and interrupted creep test were subjected to hardness and microstructural studies. The microstructural investigations were carried out by means of optical microscopy and scanning (SEM) and transmission (TEM) electron microscopy.

For optical and scanning electron (JSM-6400, JEOL) microscopy, metallographic sections were prepared by mechanical grinding, polishing down to 1- μm diamond abrasive and etching in a solution of 100 ml of ethanol, 3 g of picric acid and 1ml of HCl. For analytical TEM work thin foil specimens and extraction replicas were used as well. The thin foil specimens for TEM were prepared by mechanical grinding to have nearly 50 μm thick and then were double-jet electropolished by using an electrolyte of 950 ml of $\text{CH}_3\text{COOH}_{(\text{conc.})}$ and 50 ml of $\text{HCl}_{(\text{conc.})}$, at 13°C and 30 V. Extraction replicas were prepared from the metallographic sections, etched in a solution of 100 ml of $\text{HCl}_{(\text{conc.})}$, 10 ml of $\text{HNO}_{3(\text{conc.})}$, 100 ml of H_2O and 0.3 ml of Vogel's reagent for 1 min, then immersed one time in a solution of 0.5 g of polyvinylformal in 100 g of trichloromethane (CHCl_3) to have a thin film from the surface of the specimen, coated by nitrocellulose and finally coated by a thin film (~ 20 nm) of carbon. The nitrocellulose was removed from replicas by a solution of isoamylester. The TEM investigations were performed by a JEM-2000FX (JEOL), operated at 200 kV, in combination with an Energy Dispersive of X-ray spectrometer (EDX, Noran) and with an Electron Image Filter (EFTEM, Gatan).

RESULTS

Microstructure

The microstructure of the welded joint of P91 steel after post weld heat treatment along the axis normal to the fusion line from the weld metal to the base metal of the welded joint is shown in Fig.1(a). It was found that HAZ, which started after the fusion line (Fig. (a)), consisted of two regions; a region of ~1 mm width with tempered martensite structure of coarse prior austenite grains of an average 50 μm size was observed beside the fusion line immediately (Fig. 1(b)) and followed by a region of ~ 2.5 mm width with also tempered martensite structure but of finer prior austenite grains of an average 15 μm size (Fig. 1(c)). In HAZ the prior austenite grain size decreases gradually with increasing distance from the fusion line. In base metal (Fig. 1(d)) a tempered martensite microstructure exists with prior austenite grains of ~30 μm size.

Microhardness

The microhardness profile for the welded joint after PWHT, along an axis normal to the fusion line from the weld metal to the base metal of the welded joint is presented in Fig. 2. The microhardness was measured by using an indentation load of 10 N (HV 1); the fusion line was taken to be zero for the distance measurement. The microhardness profile reveals 4 distinct regions. Using the results of the microstructural study in Sec.3.1., these regions can be identified as follows: i) weld metal of a maximum value of hardness of 235 HV, ii) coarse-grained region of HAZ of 1 mm width and of a hardness slightly lower than that of the weld metal (~ 232 HV) iii) fine-grained region in HAZ of width of ~2.5 mm. The hardness in this region decreases with increasing distance from the fusion line and reaches its minimum value of 200 HV at a distance of ~3.5 mm from the fusion line and iv) base metal of hardness of an average value of 208 HV.

Creep Behaviour

Creep rupture strength

Figure 3 shows the experimental Creep rupture strength - Log rupture time plot at 600°C for the welded joints (WJ) of P91 steel in comparison with the experimental values of the creep rupture strength of the base metal (BM), P91 steel and of the specimens similar to the fine-grained region of HAZ (FG(BM)) of P91 steel. The solid points in the plot are from creep rupture tests and the open point is from interrupted creep test. It was found that, in general the creep rupture strength of the welded joint lies between the creep rupture strength of the base metal and that of the specimens simulated to the fine-grained region of HAZ. The creep rupture strength of the welded joint approaches the creep rupture strength of the base metal after short term creep tests (rupture time <2000 h and stress >120 MPa), while it approaches the creep rupture strength of the specimens simulated to the fine-grained region of HAZ after longer term creep tests (rupture time >4000 h and stress <110 MPa).

Fractography

Figure 4(a) shows the longitudinal section of the fracture zone of the creep specimen ruptured after 7929 h, at 600 °C and a stress of 90 MPa. It was found that the fracture of the specimen occurred in the fine-grained region of the first HAZ and by creep cavitation where wedge type cracks were observed, not only on the prior austenite grain boundaries but also on the martensite lath interfaces. Furthermore wedge type cracks were observed also in the fine-grained region of the second HAZ, as shown in Fig. 4(b), which lies on the other side of the weld metal and is far (~ 3 cm) from the highly stressed fracture zone; these cracks formed on the prior austenite grain boundaries and the martensite lath interfaces, as shown in Fig. 4(c). This confirms that the fine-grained region is the weakest part of the welded joint. Creep cavitation also occurred in the fine-grained region of HAZ in a creep test interrupted after 26035 h at 600 °C and a lower stress of 70 MPa. But in this case creep cavitation occurred by the formation of cracks on the prior austenite grain boundaries and the martensite lath interfaces which were normal to the tensile stress, as shown in Fig. 4(d).

Microstructural changes during creep

In order to study the microstructural changes of the fine-grained region of HAZ of the welded joint of P91 steel during creep at 600 °C, a comparison between the microstructure of the fine-grained region before and after creep test was made.

Inspection of thin foils of the fine grained region of HAZ of the welded joint of P91 steel, after PWHT i.e. after tempering at 760 °C for 2 h, by transmission electron microscopy, like Fig. 5, reveals that coarse, polygonal subgrains with low dislocation densities in the interiors replace the martensite structure. The average subgrain size is 0.9 µm. A measurement of the dislocation density was not made because of complexity of the martensite microstructure.

Coarse carbide particles mostly on the subgrain boundaries in addition to the precipitation of fine carbide particles within the subgrains were observed, as shown in Fig. 5.

In order to determine the types and the distribution of precipitates and to measure their composition and size distribution, quantitative analyses on carbon extraction replicas have been carried out by EDX microanalysis, EFTEM analysis, electron beam diffraction and image analysis. The carbon extraction replicas from a sample which includes the fine-grained region of HAZ, after PWHT, are shown in Fig. 6(a-b) which clearly illustrates the distribution of carbides in relation to the martensite boundaries. Table 2 shows the chemical analysis, determined by EDX, of one particle, for example, in addition to the mean value and the standard deviation of the chemical analyses of at least 7 particles for each type of carbides observed in the extraction replicas. The carbides in the tempered fine-grained region of HAZ were found to consist mainly of a dispersion of fine Cr-rich carbide particles, which it was well known as $M_{23}C_6$ in 9% Cr steel [14], concentrated at the prior austenite grain boundaries (Fig. 6(a)) and the subgrain boundaries (Fig. 5). The type of this carbide was verified by EDX microanalysis, shown in Fig. 7. The chemical analyses of these carbide particles are shown in Table 2. The particle size distribution of these carbides is shown in Fig. 8. Statistical analysis of this size distribution reveals that the average particle diameter is 90 nm.

The very fine precipitates which are important for the creep strength of P91 steel such as the spheroidal (V,Nb)-rich carbonitride, the ellipsoidal V-rich nitride and the wing-shape V-rich nitride were observed within the martensite lath subgrains as shown in Fig. 6(b). It was found that the spheroidal (V,Nb)-rich carbonitride particles appear to remain undissolved during austenitizing and act as nucleation sites for the ellipsoidal V-rich nitride during tempering, thus forming the wing-shape V-rich nitride [13]. The average particle size of these nitrides and carbonitrides is < 50 nm. The EDX spectra of these phases are shown in Fig. 9(a-b) and their chemical analyses are given in Table 2. These phases were also observed in tempered martensites of 9% Cr steels [7,13] and are known as VN and (V,Nb)(CN).

In the microstructure of the fine-grained region of HAZ of P91 steel after the long term creep test (600 °C/ 70 MPa) interrupted after 26035 h, martensite lath structure could be distinguished, as shown in Fig.4(d); but the thin foil TEM examination shown in Fig. 10 reveals that the martensite lath subgrains formed during tempering became more recovered, where the subgrains are more equiaxed, coarser and with lower dislocation densities in the interiors than before the creep test. The average subgrain size is 1.25 μm . It was found that very coarse subgrains of size > 2 μm , where dislocations were mostly recovered in their interiors, were formed discontinuously resulting in heterogeneously recovered microstructure. The subgrain boundaries were decorated by a lot of coarse carbide particles while much fewer carbide particles within the subgrains can be observed (Fig. 10). Also it should be noted that the density of carbides in the recovered region is lower than that in the surrounding martensite matrix. All these observations indicate that the interface between the recovered subgrains and martensite matrix seems to advance absorbing excess dislocations and sweeping out of carbides outside. Carbon extraction replicas of the fine-grained region of HAZ are shown in Fig. 11(a-b) and the chemical analyses, determined by EDX, of the different type of precipitates observed in these extraction replicas are revealed in Table 3. It was found that the $M_{23}C_6$ particles are coarser than before the creep test; the average particle size is about 140 nm as shown in Fig. 12. Some particles of $M_{23}C_6$ are agglomerated as shown in Fig. 11(a). Thus, the fine $M_{23}C_6$ carbide particles in the matrix present after tempering became dissolved with time during creep, in favour of the growth of more massive carbides along prior austenite grain and subgrain boundaries. Table 3 shows the chemical analysis of $M_{23}C_6$ particles. The $M_{23}C_6$ particles within the subgrains were sometimes found to be surrounded by fine particles of V-rich nitride as shown in EFTEM micrographs (Fig. 13(a-d)) and Nb-rich carbonitride. The chemical analyses of these carbonitrides are shown in Table 3. These nitrides and carbonitrides were found to be highly resistant to coarsening during creep, where their average particle size is <60 nm after 26035 h at 600°C.

The long term exposure at 600 °C results in the formation of the intermetallic compound Laves phase (Fe_2Mo), as shown in Fig. 11(b); this phase was found to form mostly on the subgrain boundaries, as shown in Fig. 10, where it can be identified by its very coarse particle size. The formation of Laves phase on the prior austenite grain boundaries and the subgrain boundaries in 9% Cr steel was also observed by Ennis et.al. [7]. Laves phase has an irregular shape and a coarse particle size of $\sim 1 \mu\text{m}$. The composition and the structure of this phase were confirmed by EDX microanalysis shown in Fig. 14 and Table 3 and by the electron beam diffraction pattern, shown in Fig. 15(a). Laves phase has the hexagonal crystal structure ($a = 0.475 \text{ nm}$, $c = 0.773 \text{ nm}$) as shown in Fig. 15(b). In addition to Laves phase plate-like precipitate particles were formed as shown in Fig. 11(b). This phase was found to be randomly distributed in the matrix, often in close association with M_{23}C_6 particles. EDX microanalysis of the particles of the new phase given in Table 3 and shown in Fig. 16, indicates that they were rich in Cr in addition to V and Nb elements. Electron diffraction pattern shown in Fig. 17, reveals that this phase has a tetragonal lattice. The above evidence coupled with the results of EDX analysis suggest that this phase is in an agreement with the modified Z phase. This phase was observed by Srang and Vodarek [14] in 12% Cr steel. In general, the particle size of this phase is greater than those of VN and Nb(CN), as shown in Fig. 11(b).

DISCUSSION

The role of Microstructural Instability of Fine-grained Region of HAZ on the Creep Behaviour

First of all, it is necessary to give some information from the literature about the microstructure of the fine-grained region of HAZ after welding and before PWHT. It was found [1] that the microstructure of the fine-grained region of HAZ of the welded joint of P91 steel consists of elongated martensite laths within fine prior austenite grains. Moreover, the M_{23}C_6 particles dissolve in the austenite matrix during welding because of its relatively low chemical affinity with carbon at the high peak temperature, while VN and (V,Nb)CN particles are fine and stable and don't dissolve into the austenite matrix during welding.

Our results show that during PWHT i.e. tempering at 760 °C for 2 h two main processes take place in the fine-grained region of HAZ of P91 steel. The first is the partial annihilation of the martensite lath structure by the formation of coarse polygonal subgrains from the original elongated martensite laths and the recovery of dislocations within these subgrains. The second process is the formation of coarse carbide particles of M_{23}C_6 mostly on the subgrain boundaries in addition to the precipitation of fine particles of VN and Nb(CN) mainly within the subgrains. By tempering of martensite of low carbon low alloy steel, it was found that the interfacial energy associated with the high density of lath boundaries is the driving force for the growth of martensite lath subgrains, the strain energy associated with the fine dislocations in laths is the driving force for the recovery of dislocations and the supersaturation of martensite with carbon atoms is the driving force for the precipitation and coarsening of carbides [15].

The microstructural changes in the fine-grained region of HAZ of P91 steel which occurred during the long term creep test (600°C / 70 MPa), which was interrupted after 26035 h can be summarised as follows:

- continuous recovery of the subgrains by the formation of coarser, more well equiaxed subgrains with lower dislocation densities in the interiors than before the creep test. The recovery of subgrains seems to occur heterogeneously. The growth of the martensite lath subgrains during creep, under the action of the stress, may occur by the migration of high angle subgrain boundaries, which are strongly pinned by the fine carbide particles and the annihilation of the other subgrain boundaries by the recovery of dislocations.
- coarsening and agglomeration of M_{23}C_6 particles.

- stability of the fine V-rich nitride and Nb-rich carbonitride particles and additional precipitation of very fine particles of these nitrides and carbonitrides on the $M_{23}C_6$ particles.
- formation of coarse particles of Laves phase on the prior austenite grain boundaries and the subgrain boundaries.
- precipitation of Z phase, which is rich in Cr, V and Nb, often at the vicinity of $M_{23}C_6$ particles.

The lower creep resistance of the welded joint in comparison with the base metal for P91 steel after long term creep test at 600 °C is due to the low creep resistance of the fine-grained region of its HAZ. This could be confirmed by the followings. Creep cavities have formed on the prior austenite grain and subgrain boundaries only in this region as mentioned previously in the section of *fractography*. The specimens similar to the fine grained region of HAZ have the lowest creep resistance in comparison with the base metal and the welded joint (see Fig. 3). The low creep resistance of the fine grained region of HAZ is due the followings:

- 1) softening during creep results mainly from the growth of the martensite lath subgrains and also from the recovery of dislocations within these subgrains. It was found that the creep strength of 9 % Cr steels is inversely proportional to the subgrain size and also to the dislocation density in the subgrain interior [9].
- 2) disappearance of fine $M_{23}C_6$ carbide particles at the martensite lath subgrain boundaries, because of the coarsening and agglomeration of these particles during creep, results in an increase in the rate of growth of the subgrains i.e. an increase in the rate of softening. Furthermore, the coarsening and agglomeration of the intragranular $M_{23}C_6$ particles results in an increase in interparticle spacing and a decrease in particle strengthening.
- 3) the precipitation of the fine particles of V-rich nitride and Nb-rich carbonitride in association with the coarser $M_{23}C_6$ particles prevents their contribution to particle strengthening.
- 4) the formation of the intermetallic compound Laves phase, Fe_2Mo consumes much Mo from the matrix, decreases its contribution to the solid solution strengthening and so results in a reduction in the creep rupture strength of the matrix. It was found that Mo addition improves the creep properties of 9% Cr steels through solid solution strengthening [16,17]. Furthermore, the presence of this brittle phase on the prior austenite grain boundaries and the subgrain boundaries accelerates creep cavitation.
- 5) the formation of Z phase of Cr(V,Nb)N reduces the creep strength by the consumption of precipitation strengthening elements such as V, Nb and Cr from the matrix. The reduction in strength is due to that Cr(V,Nb)N particles are coarser than VN and Nb(CN) particles. It was found that the precipitation of fine spherical particles of Nb(CN) and ellipsoidal particles of VN were shown to be effective obstacles against dislocation glide resulting in an increase in creep rupture strength in high nitrogen (~0.055 wt.%) 10XCrMoNbV steel [13]. Also P91 steel has the same high nitrogen content (see Table 1).

The last five factors mentioned above, generally play the same role, but with different rates, in reducing the creep resistance of the fine-and the coarse-grained regions of HAZ, the base metal and the weld metal of the welded joint of P91 steel. It was observed that the main differences between these regions of the welded joint are the prior austenite grain size and the peak temperature during welding. The role of these two factors is going to be discussed in the next sections.

The Role of Prior Austenite Grain Size on the Creep Behaviour

It was observed that at low stresses and long term creep tests, the recovery of martensite laths in 9 % Cr steel occurred heterogeneously, where a significantly recovered region was observed at the vicinity of prior austenite grain boundaries, while the microstructure within the grains is still fine [8]. Heterogeneous recovery of martensite laths was also observed in

the fine-grained region of HAZ of P91 steel, as shown in Fig.10. The preferential recovery of subgrains at the vicinity of prior austenite grain boundary during long term creep deformation is due to the higher internal stress, introduced by martensitic transformation, at the vicinity of the grain boundary than within the grain interior. This stress is the important factor to promote recovery of tempered martensite microstructure. It seems that an effect of higher internal stress at the prior austenite grain boundary on microstructural change may be pronounced in long term creep test, since the applied stress is lower than that in the short term creep test. The preferential recovery of subgrains at the vicinity of prior austenite grain boundaries promotes the onset of tertiary creep, since creep deformation is mainly dependent on a deformation at the vicinity of the prior austenite grain boundaries [8].

It was found in martensitic 12 % Cr steel that creep cavities lying on transverse prior austenite grain boundaries play the dominant role in the creep rupture process where these cavities are larger and more closely spaced than those on the subgrain boundaries within the prior austenite grains [6].

The fine prior austenite grains in the fine-grained region of HAZ of the welded joint of P91 steel means a high grain boundary area of prior austenite per unit volume; this high grain boundary area of prior austenite accelerates the rate of growth of the martensite lath subgrains and the rate of recovery of dislocations within these subgrains resulting in an increase in the rate of softening and a decrease in the creep resistance. Also the fine prior austenite grain size means a large number of preferred sites for the formation of large and closely spaced cavities during creep which enhance creep cavitation. The formation of creep cavities on transverse prior austenite grain boundaries were observed only in the fine-grained region of HAZ of the welded joint of P91 steel, especially in the long term creep test which was interrupted after 26035 h at 600°C and a low stress of 70 MPa, as shown in Fig. 4(d).

The Role of Peak Temperature during Welding on the Creep Behaviour

The low peak temperature during welding means the low transformation temperature of austenite to martensite in heat treatable steels. The lower transformation temperature of austenite to martensite resulted in finer prior austenite grain size and smaller number of dislocations stored after the transformation in comparison with the higher transformation temperature, as found in 9 % Cr steels [18]. Although the fine-grained region of HAZ of the welded joint of P91 steel, which resulted from the low peak temperature in this region during welding has the finest prior austenite grain size, it has the softest martensite matrix in comparison with the other regions as shown in the microhardness profile (Fig. 2). This may be due to the smallest number of dislocations stored after martensitic transformation in this region. Therefore the fine-grained region of HAZ has the highest rate of recovery of the martensite lath subgrains during creep and the lowest creep resistance.

CONCLUSIONS

It was concluded that the main microstructural changes which occurred in the fine-grained region of HAZ of the welded joint of P91 steel during the long term creep test (600°C / 70 MPa), which was interrupted after 26035 h are:

- coarsening of the martensite lath subgrains and recovery of dislocations within these subgrains.
- coarsening and agglomeration of $M_{23}C_6$ particles.
- formation of coarse particles of Laves phase on the prior austenite grain boundaries and the subgrain boundaries.

- precipitation of Z phase, which is rich in Cr, V and Nb and also V-rich nitride and Nb-rich carbonitride, often in close association with $M_{23}C_6$ particles.

The most effective factors reducing the creep rupture strength of the fine-grained region of HAZ of the welded joint of P91 steel, in relation to the coarse-grained region of HAZ, the base metal and the weld metal of the welded joint are the finer prior austenite grain size of the fine-grained region which accelerates the rate of growth of martensite lath subgrains increasing the rate of softening and enhances creep cavitation and the softer martensite matrix in the fine-grained region which results from the lower peak temperature in this region during welding.

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Table 1: Chemical analysis of P91 steel.

Element, wt. %										
C	Si	Mn	Cr	Mo	V	Nb	Ni	P	S	N
0.104	0.27	0.46	8.17	0.90	0.194	0.064	0.16	0.014	0.003	0.055

Table 2: Chemical analyses by EDX of different types of particles observed in the extraction replicas of the fine-grained region of HAZ of P91steel after PWHT.

Element	Atomic %						
	Cr-rich carbide ($M_{23}C_6$)			V-rich nitride (VN)			(V,Nb)-rich carbonit. (V,Nb)CN)
	one particle	mean value	standard deviation	one particle	mean value	standard deviation	one particle
Cr	64.30	61.53	1.94	15.24	14.63	2.28	9.20
Fe	28.30	28.36	1.07	3.17	4.84	2.38	6.99
V	1.20	1.98	2.00	75.20	71.23	4.70	47.40
Nb	1.30	1.67	0.68	6.39	8.97	3.41	36.40
Mo	4.90	6.47	0.91	0.00	0.33	0.61	0.00

Table 3: Chemical analyses by EDX of different types of particles observed in the extraction replicas of the fine-grained region of HAZ of P91steel after long term interrupted creep test at 600 °C.

Element	Atomic %												
	Cr-rich carbide (M ₂₃ C ₆)			V-rich nitride (VN)			Nb-rich carbo. (Nb(CN))	Z phase (Cr(V,Nb)N)			Laves phase (Fe ₂ Mo)		
	OP*	MV*	SD*	OP	MV	SD	OP	OP	MV	SD	OP	MV	SD
Cr	69.7	68.6	1.97	15.2	13.0	2.23	1.2	36.6	38.5	3.01	7.3	8.1	0.53
Fe	22.4	22.3	2.33	4.6	3.6	0.95	1.9	3.2	4.3	0.77	49.6	48.8	0.51
V	0.9	1.1	0.87	74.5	73.7	0.96	9.6	33.4	38.8	5.11	0.3	0.5	0.60
Nb	0.8	1.0	0.42	5.2	8.8	3.11	85.3	26.0	18.0	5.44	5.2	5.0	1.07
Mo	6.1	7.0	0.95	0.5	0.9	0.46	2.0	0.8	0.4	0.26	37.7	37.6	1.82

*OP: one particle, MV: mean value and SD: standard deviation.

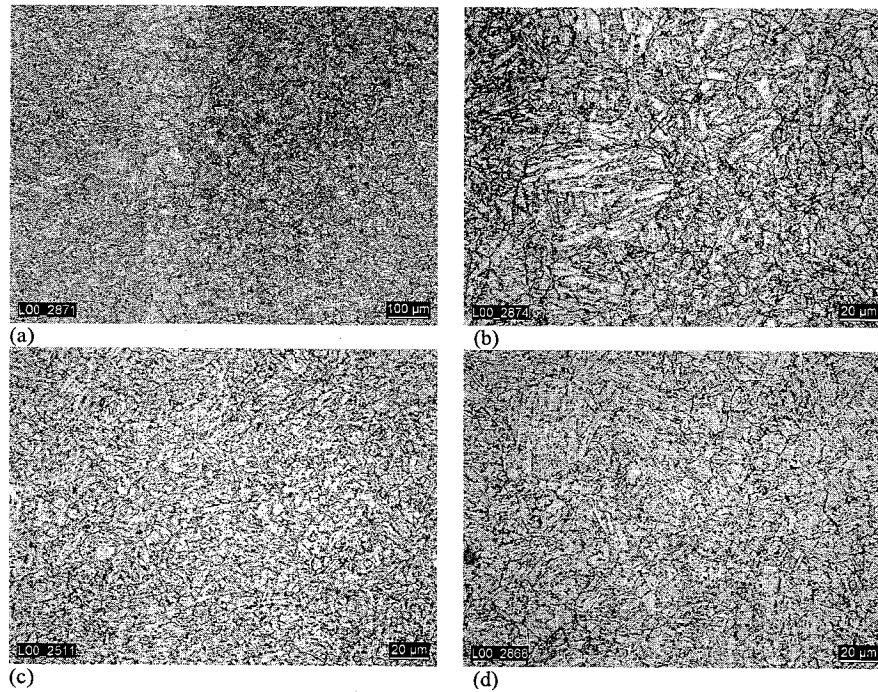


Fig. 1: Microstructures of the welded joint of P91 steel after PWHT: (a) weld metal + HAZ, (b) coarse-grained region of HAZ, (c) fine-grained region of HAZ, (d) base metal.

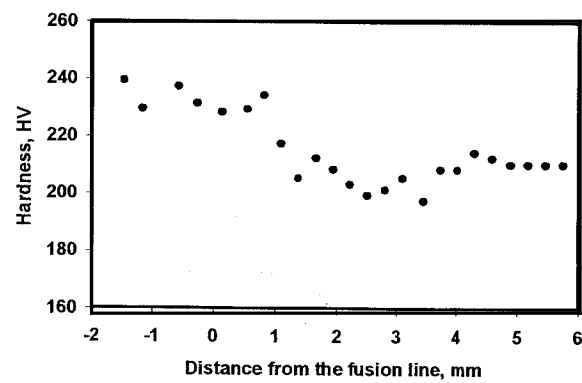


Fig. 2: Microhardness profile of the welded joint of P91 steel after PWHT.

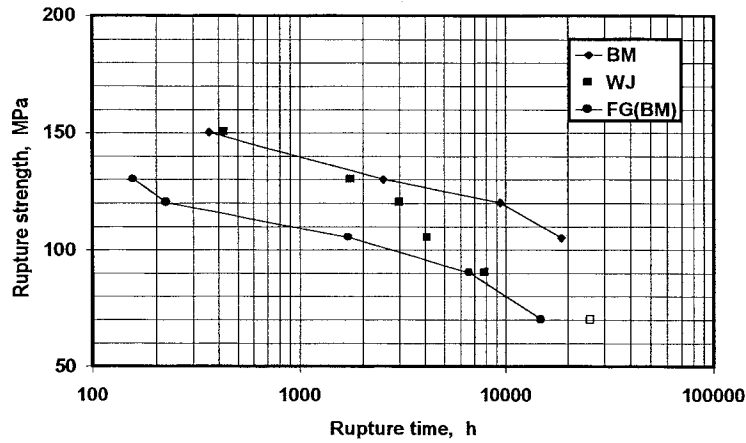


Fig. 3: Creep rupture strength - Log rupture time plot of P91 steel at 600 °C.

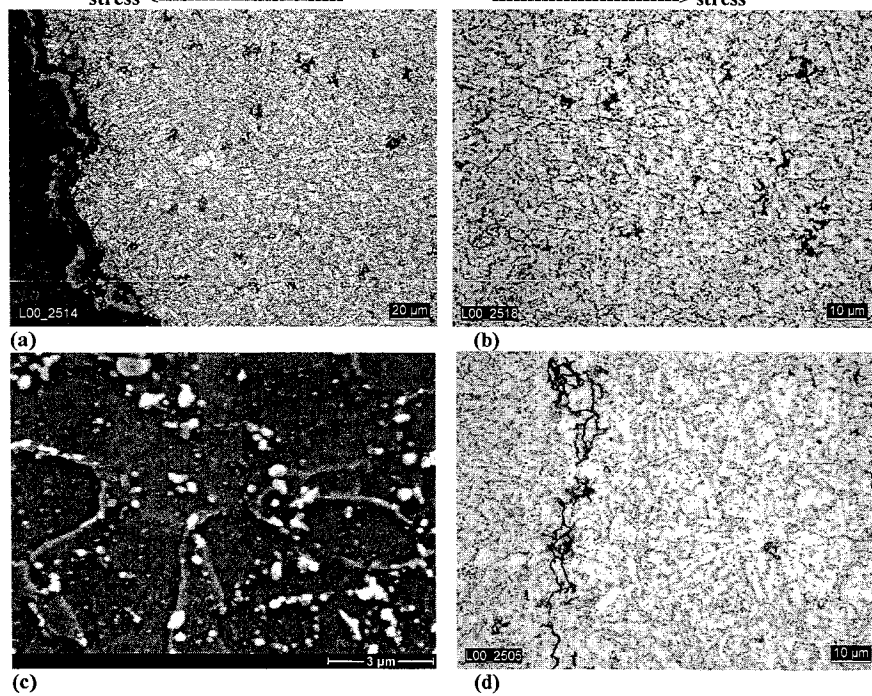


Fig. 4(a-d): Microstructures of the longitudinal sections of the creep specimens of the welded joint of P91 steel:
a) optical micrograph of the fracture zone in fine-grained region of the first HAZ after creep test at 600°C and 90 MPa, (b) optical micrograph of the fine-grained region of the second HAZ after creep test at 600°C and 90 MPa, (c) SEM micrograph of the fine-grained region of the second HAZ after creep test at 600°C and 90 MPa, (d) optical micrograph of the fine-grained region of HAZ after interrupted creep test at 600°C and 70 MPa.

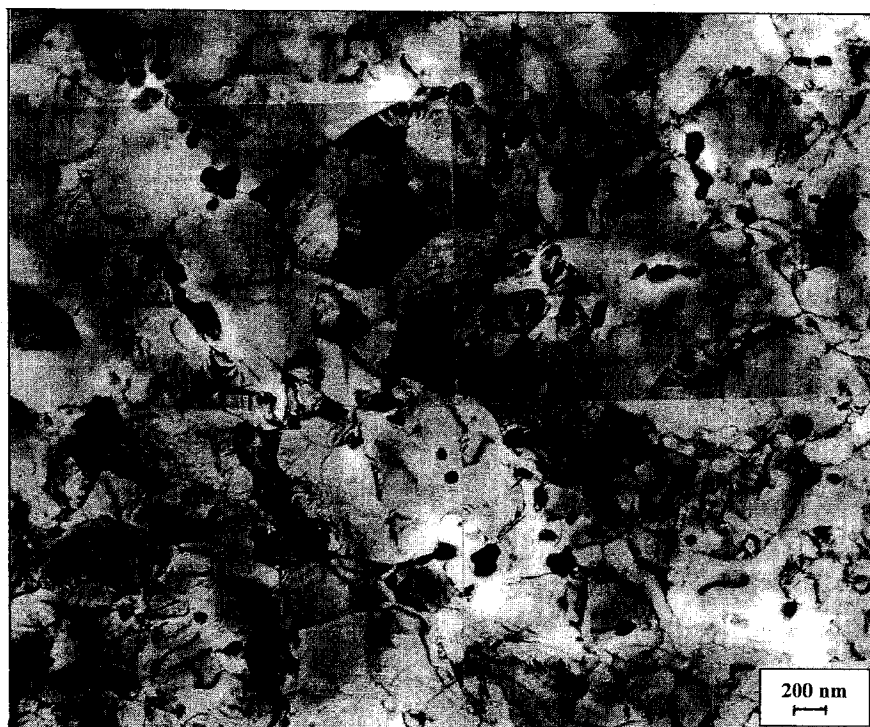
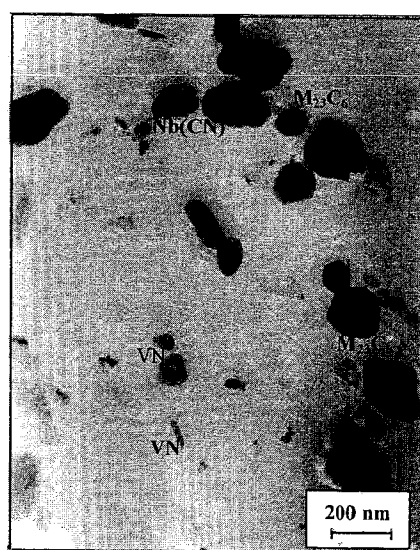


Fig. 5: TEM thin foil micrographs of the fine-grained region of HAZ of P91 steel after PWHT.



(a)



(b)

Fig. 6(a-b): Carbon extraction replicas of the fine-grained region of HAZ of P91 steel after PWHT.

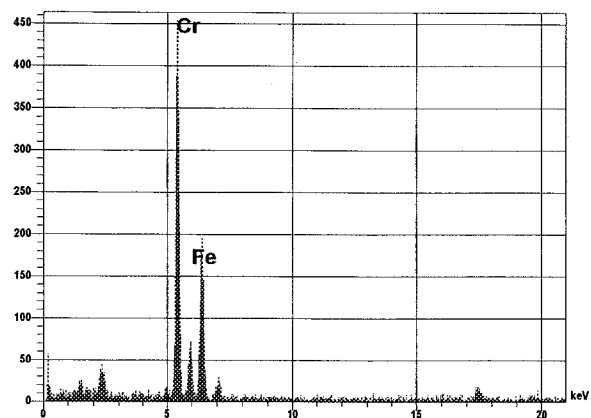


Fig. 7: EDX spectrum of Cr-rich carbide, $M_{23}C_6C$

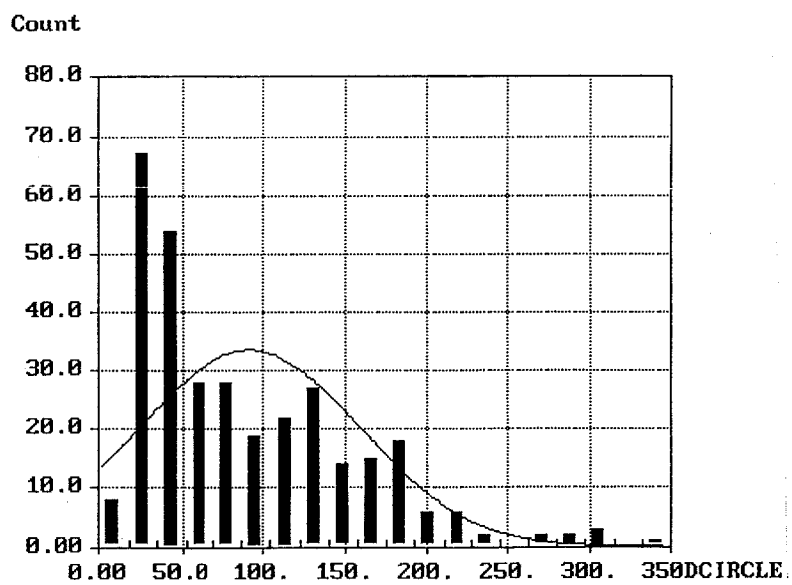


Fig.8: Particle size distribution of Cr-rich carbide, $M_{23}C_6C$.

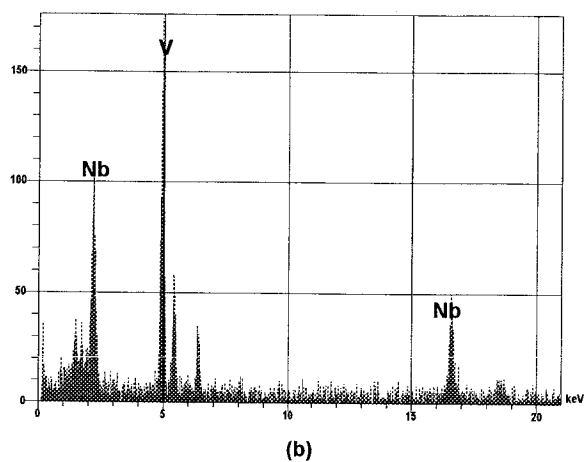
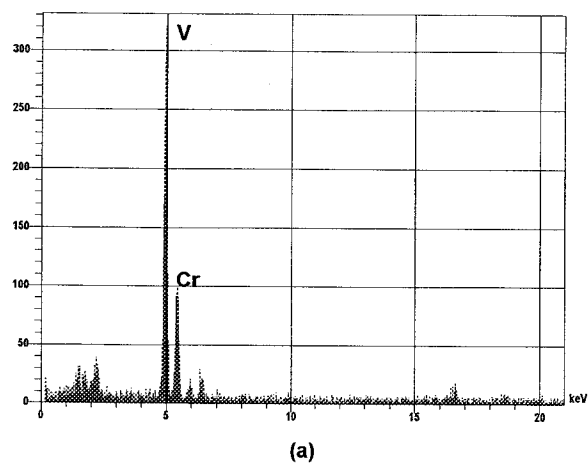


Fig. 9: EDX spectra of : (a) V-rich nitride, VN, (b) (V,Nb)-rich carbonitride, (V,Nb)CN.

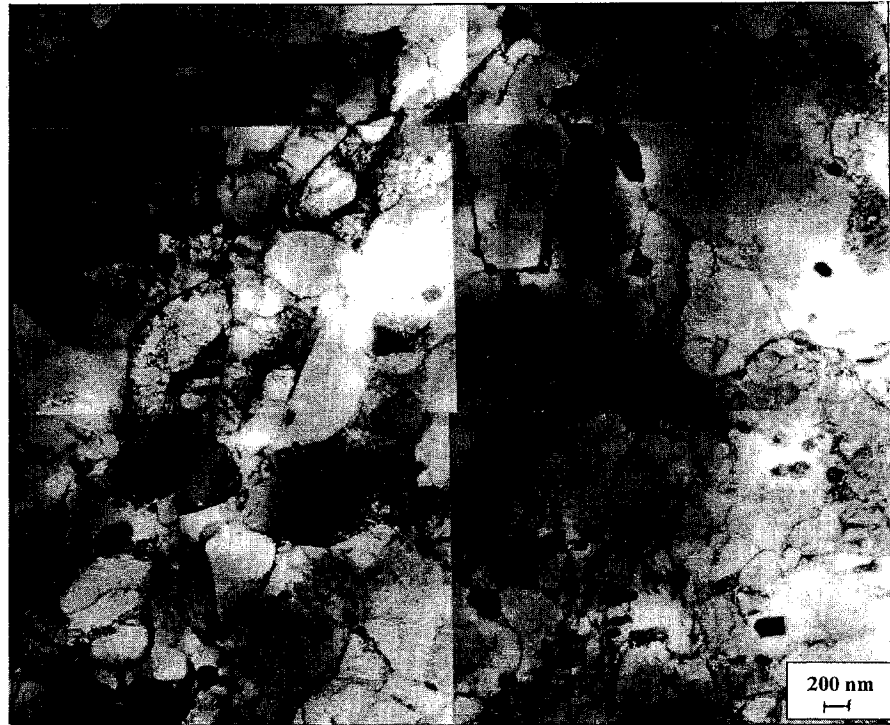


Fig. 10: TEM thin foil micrographs of the fine-grained region of HAZ of P91 steel after the interrupted long term creep test at 600°C and 70 MPa.

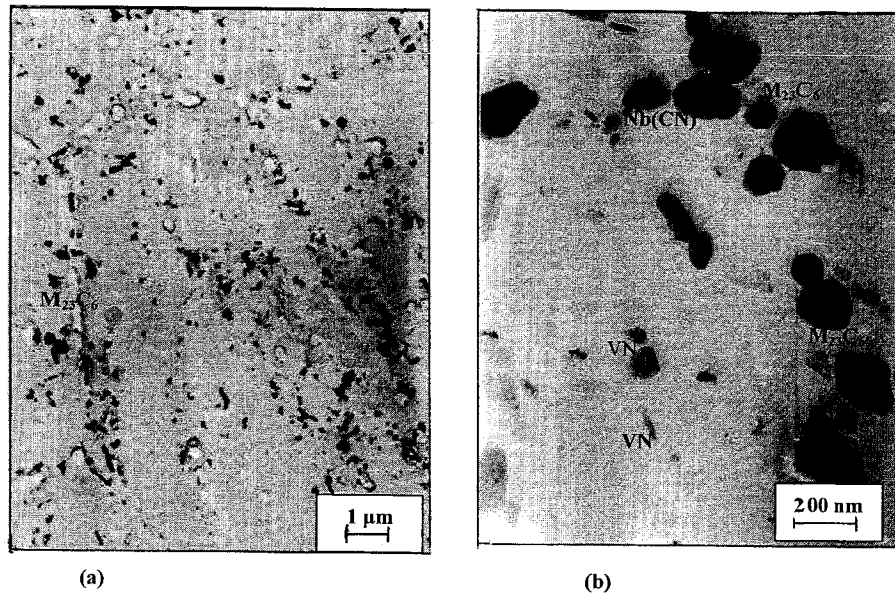


Fig. 11(a-b): Carbon extraction replicas of the fine-grained region of HAZ of P91 steel after the interrupted long term creep test at 600°C and 70 MPa.

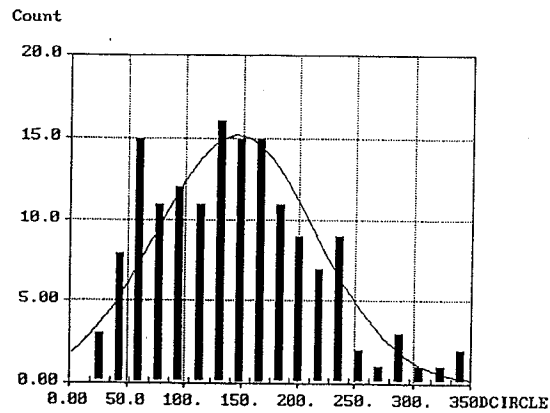


Fig. 12: Particle size distribution of the Cr-rich carbide, $M_{23}C_6$ after the interrupted long term creep test at 600°C and 70 MPa.

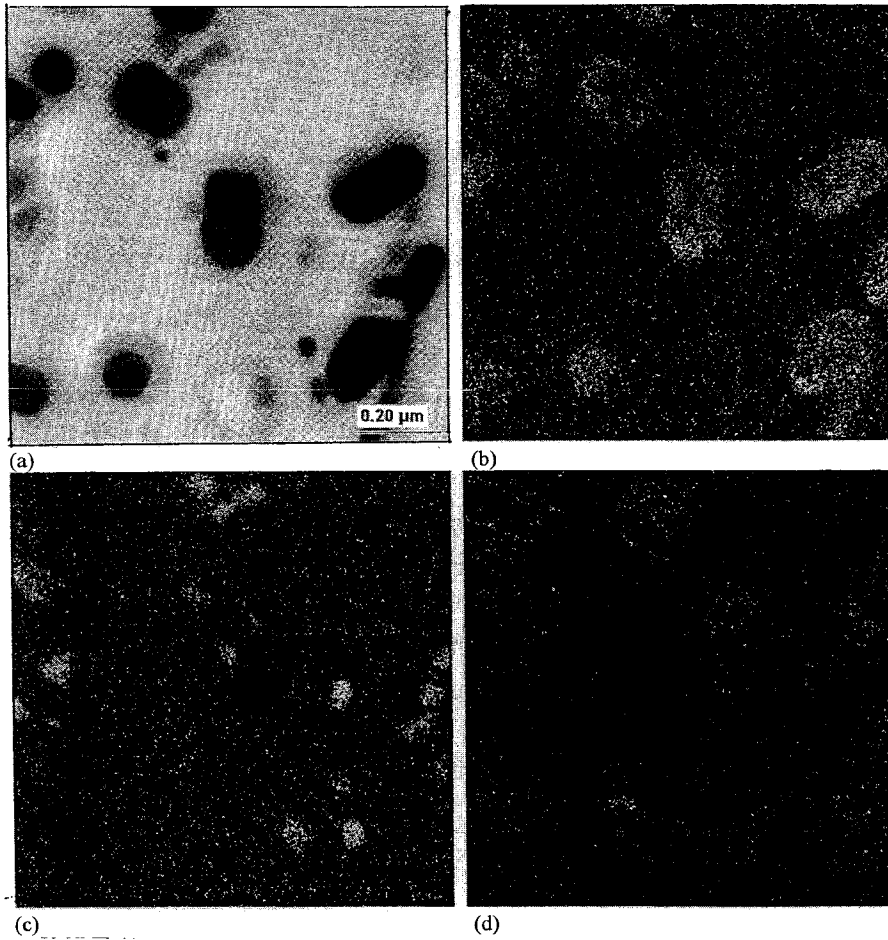


Fig. 13(a-d): EFTEM-investigation on the extraction replicas of the fine-grained region of HAZ of P91 steel after the interrupted long term creep test at 600°C and 70 MPa: (a) TEM bright field, (b) elemental map of Cr, (c) elemental map of V, (d) elemental map of Mo.

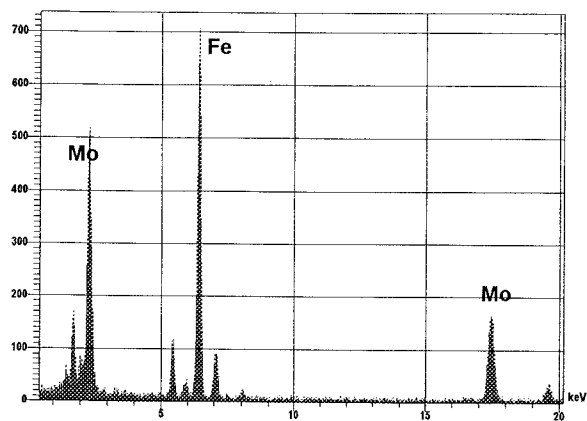
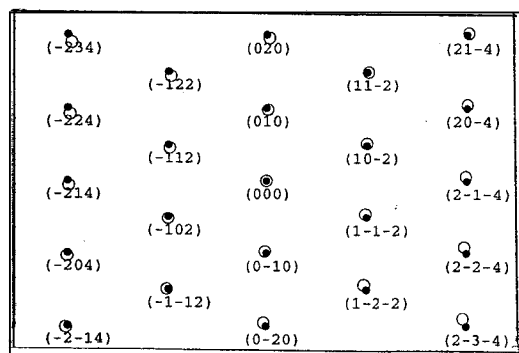


Fig. 14: EDX spectrum of Laves phase.



(a)



(b)

Fig. 15(a-b): Electron diffraction pattern of Laves phase : (a) a selected area electron diffraction pattern in the [201] orientation, (b) superposition of the theoretical electron diffraction pattern with the experimental one.

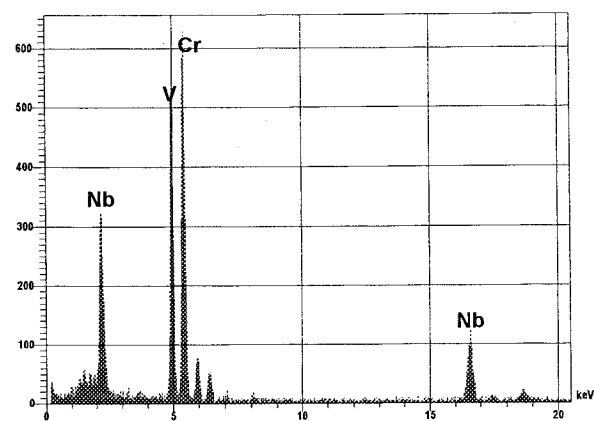


Fig. 16: EDX spectrum of Z phase.



Fig. 17: A selected area electron beam diffraction pattern of Z phase.

SOME MECHANICAL PROPERTIES OF MO ALLOYS USED FOR DIVERTOR STRUCTURAL MATERIAL

A.M.. Nasreldin,¹⁾ G. Pott,²⁾ M. Rödiger²⁾

Abstract

Mo – alloys are candidate structural materials to be used with divertor plates in future fusion reactors. During operation of a fusion reactor these materials will be subjected to irradiation hardening and subsequent embrittlement is expected. Therefore it is necessary to study the influence of fast neutrons (irradiation in a research reactor) on the mechanical properties. Five different materials had been irradiated at 75, 400 and 750 °C up to a neutron fluence of 1 dpa. Neutron induced embrittlement was manifested e.g. by a shift in the impact transition curves to higher temperature ranges and a decrease in the upper shelf energy. This effect is less with increasing irradiation temperatures. Mo/ Re alloys displayed the highest and TZM the lowest impact properties in the pre – and post irradiation condition. The poor impact toughness of TZM can be a result of the large grain size and serration of interstitials to the grain boundaries. SEM fractography was used to correlate the impact properties with fracture surface morphology. For the characterisation of the material additional tests had been carried out:

Tensile tests up to 800 °C, dynamic fracture toughness up to 450 °C and metallographic examination

1. Introduction

One of the main design concepts under development for divertor target-plates (Fig.1) to be used in fusion reactors (e.g. ITER) is based on high Z material, e.g. W, Mo, Mo/Re alloys and TZM. The divertor is a critical component of a fusion device and structure materials must be able to resist intensive neutron and heat fluxes. The heat flux can turn on a very high and localised heat load in case of disruptions or deposition of energy from runaway electrons. Thermal calculation for the ITER concept shows, that temperatures of 400 °C - 700 °C could be reached. During operation of a fusion reactor with those materials hardening and subsequent embrittlement are expected by high energy neutron flux. Therefore it is necessary to study the influence of these conditions by fracture mechanic examination and by simulation of these conditions in irradiation experiments in a fission reactor.

Several materials (Fig.2) had been selected and tested for getting some mechanical properties for unirradiated and irradiated material. The materials are:

Mo	mechanical properties
Mo (Z6)	second supplier
TZM	mechanical properties
Mo-5Re	fracture mechanic properties
Mo-41Re	fracture mechanic and mechanical properties

1

1) A.E.A., Cairo Metallurgy Department R.C. Inchass

2) Forschungszentrum Jülich (FZJ) BD.HZ

Mechanical Properties

For measuring the embrittlement of the material, different methods and samples (fig 3) had been selected.;

- ◆ tensile strength (samples 4,5 mm Ø and 50 mm long)
- ◆ ductile to brittle transition temperature (DBTT) by 3 point bending tests. (samples 2x2 mm² and 50mm long).
- ◆ Impact strength, (notched samples 6x6 mm² and 44 mm long, DVMK sample).

The irradiation of the samples Fig.:4 had been carried out in the HFR (Petten) research reactor at different temperatures and neutron fluences. The nominal conditions had been:

- | | |
|------------------------|------------------------|
| ◆ Irradiation facility | NEMESIS Nr. 1-6 . |
| ◆ Sample carrier | ~ 30 mm Ø, 400 mm long |
| ◆ Temperature | 75, 400 and 750 °C. |
| ◆ Neutron fluence | equiv. 0,2 and 2,0 dpa |
| ◆ Irradiation time | 25 and 120 fpd. |

The characteristic **structure** of the tested TZM material is shown in Fig. 5 (micrographs). For all other materials the structure was similar.

The **tensile strength** was measured at different temperatures. The highest values had been recorded from Mo-Re and TZM samples. (Fig.: 6)

The values of the **impact strength** measurements are plotted in Fig.:7 and 8. For the unirradiated material Mo-41Re (DSR) an impact strength of about 280 J cm⁻² (50 °C), for Mo 140 J cm⁻² (200 °C) was recorded and for Mo-41Re and TZM the upper shelf was not reached up to the maximum testing temperature; this means higher embrittlement at temperatures below 400 °C. During neutron irradiation the embrittlement is increasing at an irradiation temperature of 75 °C. But with increasing irradiation temperatures an annealing effect was detected.

Similar results had been measured by **3 point bending** tests. (Fig.:9). Mo and Mo-Re had the lowest transition temperature for unirradiated test samples. The difference of ductile/brittle transition temperature (Δ DBTT) is increasing with increasing neutron fluence. But at elevated irradiation temperature an annealing effect was observed. For Mo-41Re this effect starts at 400 °C or even below. The recrystallised material (REC) was more sensitive to neutron embrittlement than the deformed and stress relieved (DSR) material. More information are given in Fig.:10.

Fracture Mechanics Investigations

High heat rate loading in divertors may cause unstable crack propagation leading to a spontaneous failure of the components. Cracks may be also created during the production process or develop during the operation of the component. For the assessment of cracked components, the knowledge of dynamic and static fracture mechanics data (K_{IC} , K_{Id} for Mo and Mo alloys are reacquired.

For fracture toughness according to ASTM E-399 the samples shall be pre-cracked by fatigue. This pre-cracking is achieved by a stepwise increase of the upper load in the fatigue cycles. But this method failed due to their brittleness. Two alternative methods were tried.:

1. The upper load of the fatigue cycle was increased continuously until a first crack propagation could be monitored by a DC potential drop method DCPD.
2. Fracture toughness was measured for different saw cuts with widths between 0,1 and 0,5 mm. This method is often used for ceramic materials. Below a certain threshold, the measured fracture toughness is expected to be independent on the notch root radius. The corresponding stress intensity factor is assumed to be the real fracture toughness.(Fig.:11)

The influence of **crack tip** (saw cut vs. fatigue crack) can be seen in Fig.:12. In fracture mechanics tests with **TZM** it should be sufficient to use fine machined notches instead of fatigue pre-cracks. For **Mo-5Re** it is preferable to use fatigue cracks instead of machined notches. But for the narrowest saw cut of 0,1 mm ($\sigma = 0,5$ mm, $\sqrt{\sigma} = 0,25$ mm^{1/2}) the value of the pre-cracked samples is nearly reached.

Dynamic fracture toughness had been measured by impact bending tests. The sample preparation by pre-cracking failed for both materials. From the experience of the static fracture mechanics tests which allow fine saw cuts of 0,1 mm instead of pre cracked samples. It was assumed that the same holds for dynamic fracture toughness $K_{I,d}$ test. Therefore part of the samples were cut with a thin diamond wire of 0,08 mm thickness. The depth of these slots was 2-3 mm. The other samples were produced with ISO-V-notches which were sharpened by a razor blade in addition. The results are plotted in Fig.:13,14. Two surprising facts are found from the results:

- ◆ The gained values of $K_{I,d}$ for samples with a saw cut are about 30% higher than those for the samples with ISO-V notches.
- ◆ The calculated values of dynamic fracture toughness are 3 to 4 times as high as the values of the static fracture toughness.

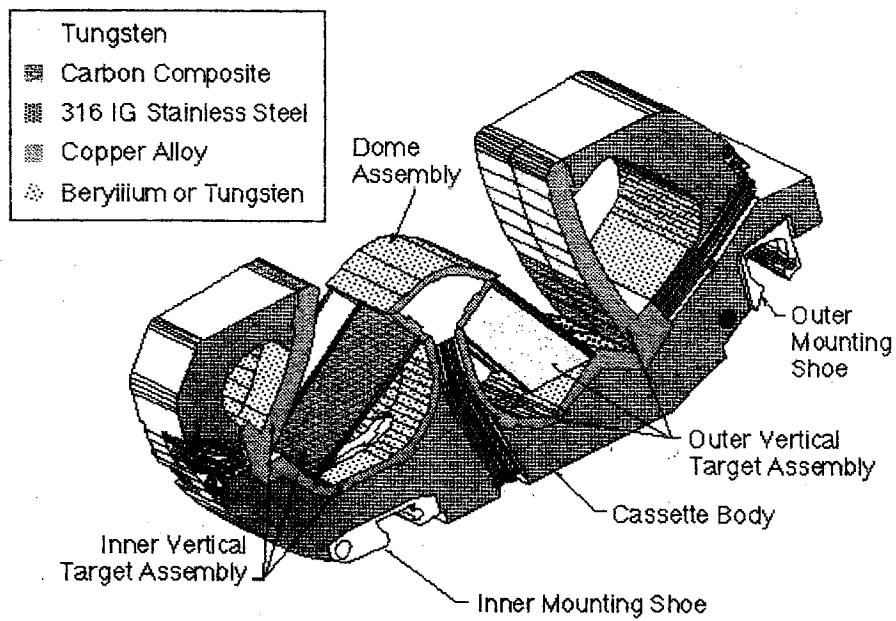
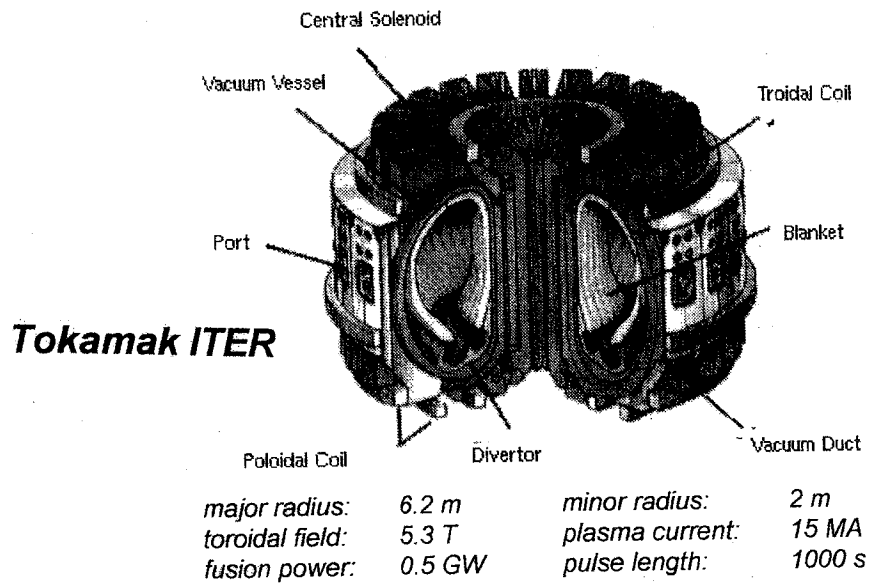
The first fact may be explained by a different kind of stress state under static and dynamic loading conditions. The conservative situation which in the static tests is reached for a saw cut of 0,1 mm width, may no longer be given under dynamic loading conditions.

The second fact surprises, because $K_{I,d}$ was expected to be lower than $K_{I,C}$. This discrepancy may partly be explained from different planes of crack propagation for both types of samples relatively to grain orientation. The measured values for static fracture toughness fit quite well with results found in other research centres for the same material. For TZM dynamic fracture toughness values of 55 MPa m^{1/2} were reported in literature. The reason for the high values of $K_{I,d}$ compared to $K_{I,C}$ is not yet understood. For understanding this discrepancies, a second set of samples with different crack plane orientation should be investigated.

The microstructure of some of the samples is documented in Fig.:15,16. The crack propagation and the crack surface shows no abnormal micro structure.

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Drawing: US Home Team
 Materials Selection: NET 180435

Fig.:1 Prototype Divertor Cassette Configuration

CHEMICAL COMPOSITION OF MO AND MO-ALLOYS
(ppm)

Material	Mo	Z6	TZM	Mo-5Re	Mo-41 Re
C	<10	<30	100	10	6
O ₂	20	<50	295	5	41
N ₂	<5	<10	25	3	<5
Si	<25	<50	<25		<25
Fe	39	<80	85		113
Ni	<5	<30	22		6
Al	<5	<20	<5		<10
Zr		300	560	8	
Cr		<30			36
W		<220			
Ti %			0,49		
Re %				5,1	40,8
Mo %	balance	balance	balance	balance	balance

Fig.:2

==GP=C12/02==

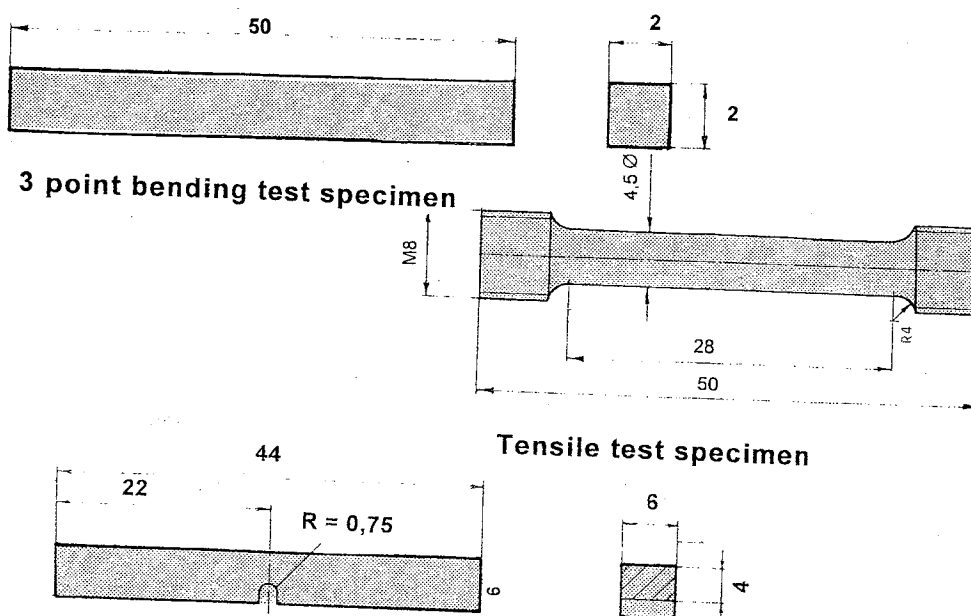


FIG.:3 SPECIMENS FOR TESTING MECHANICAL PROPERTIES

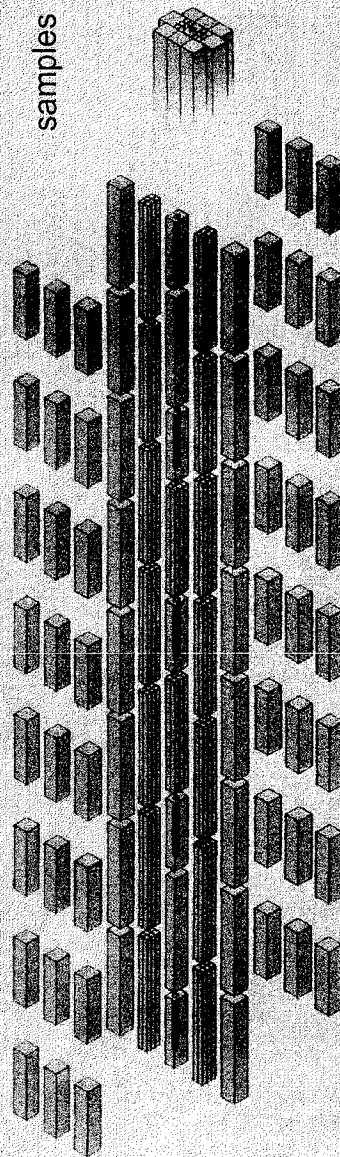
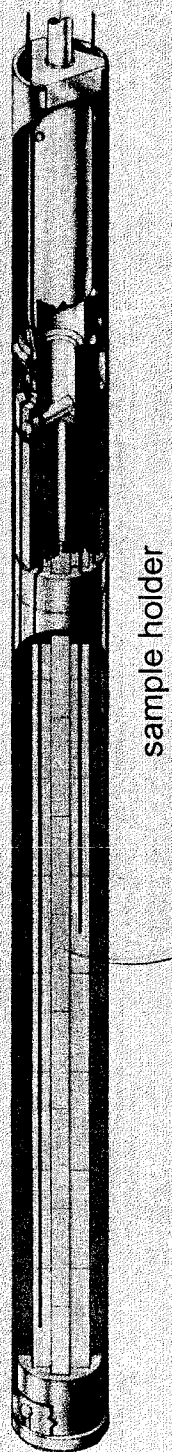
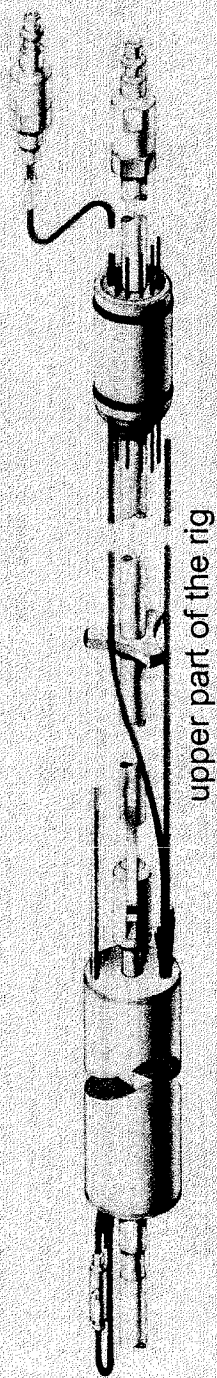
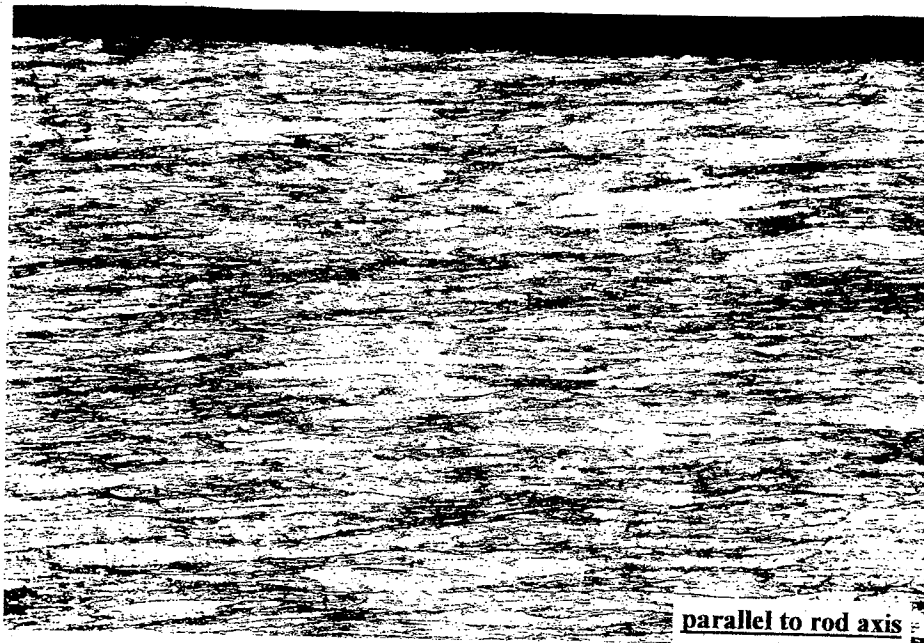


Fig.:4 General arrangement of the irradiation facility HFR



MICROGRAPHS TQM OF A ROD

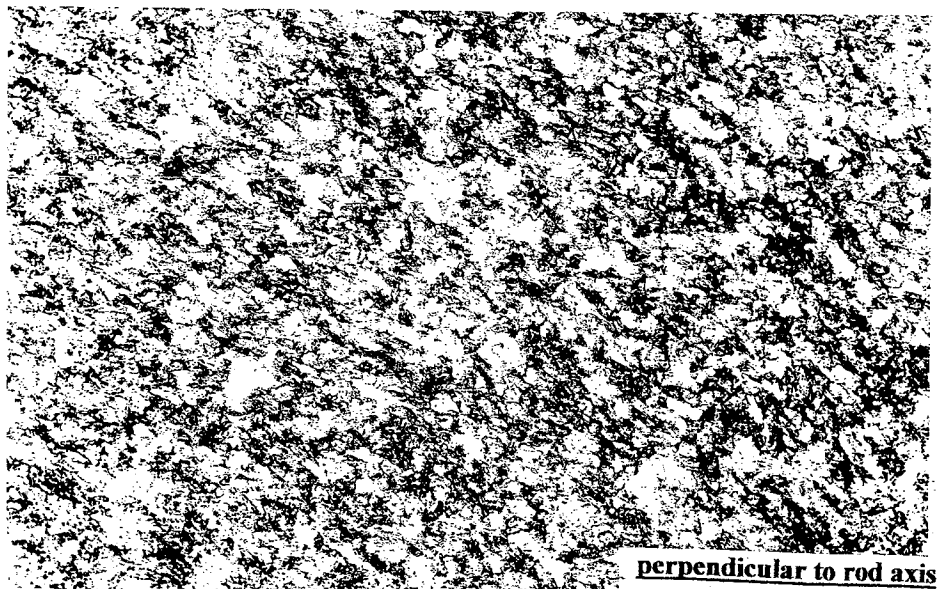


Fig.:5

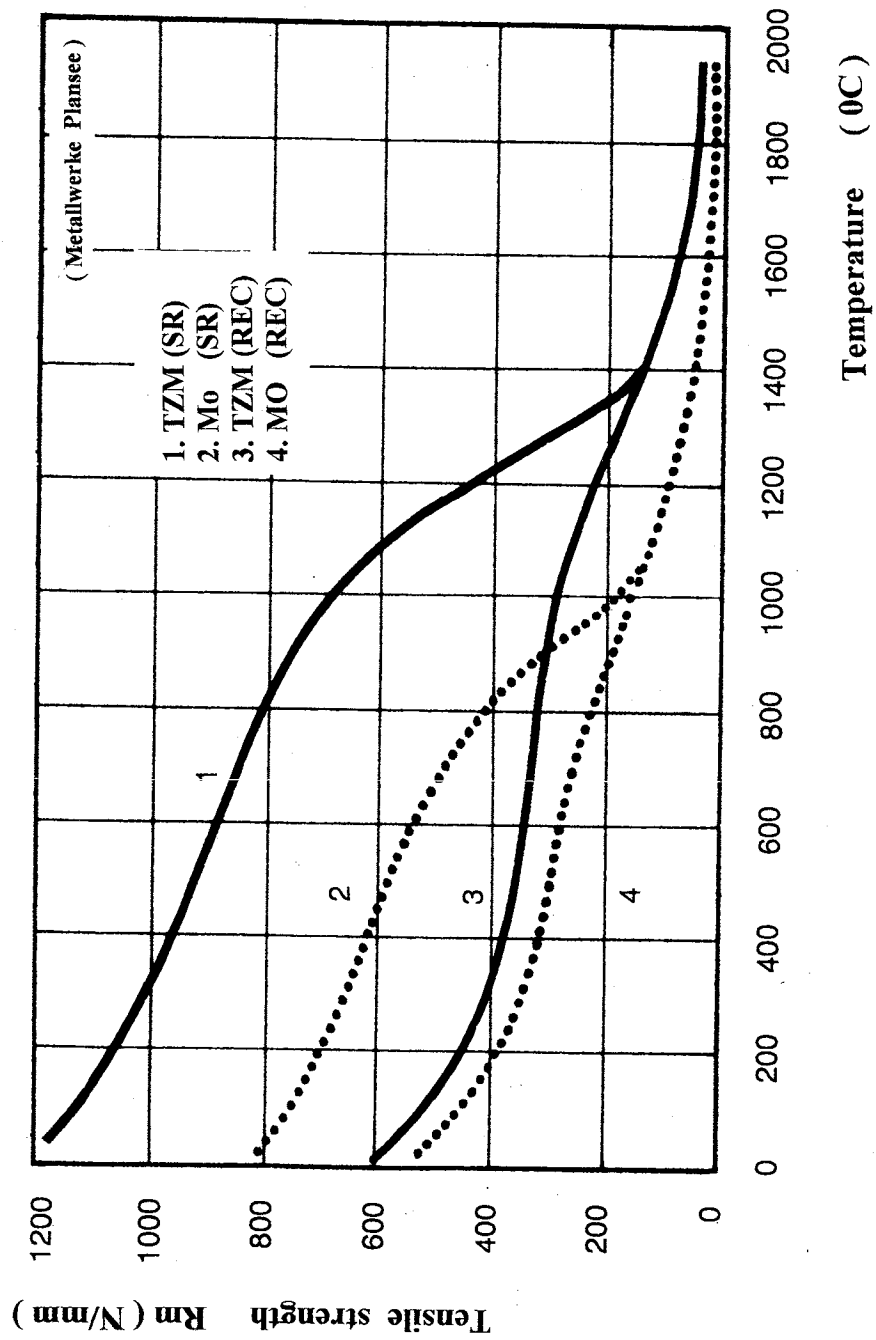


Fig.:6 Tensile strength versus temperature for 1mm thick Mo and TZM sheets

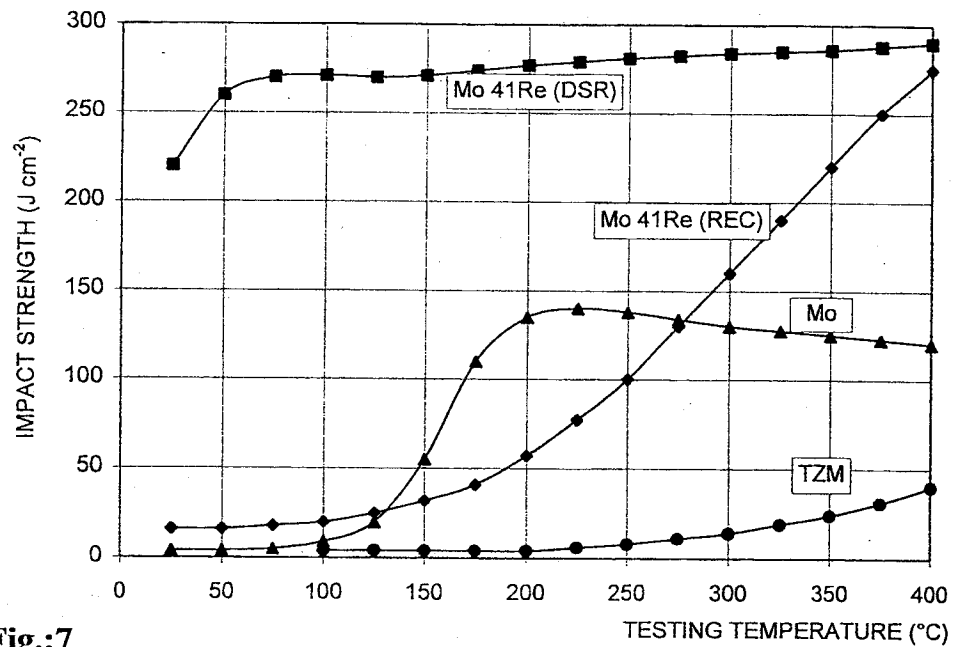


Fig.:7
IMPACT STRENGTH OF Mo AND Mo-ALLOYS (UNIRRADIATED)

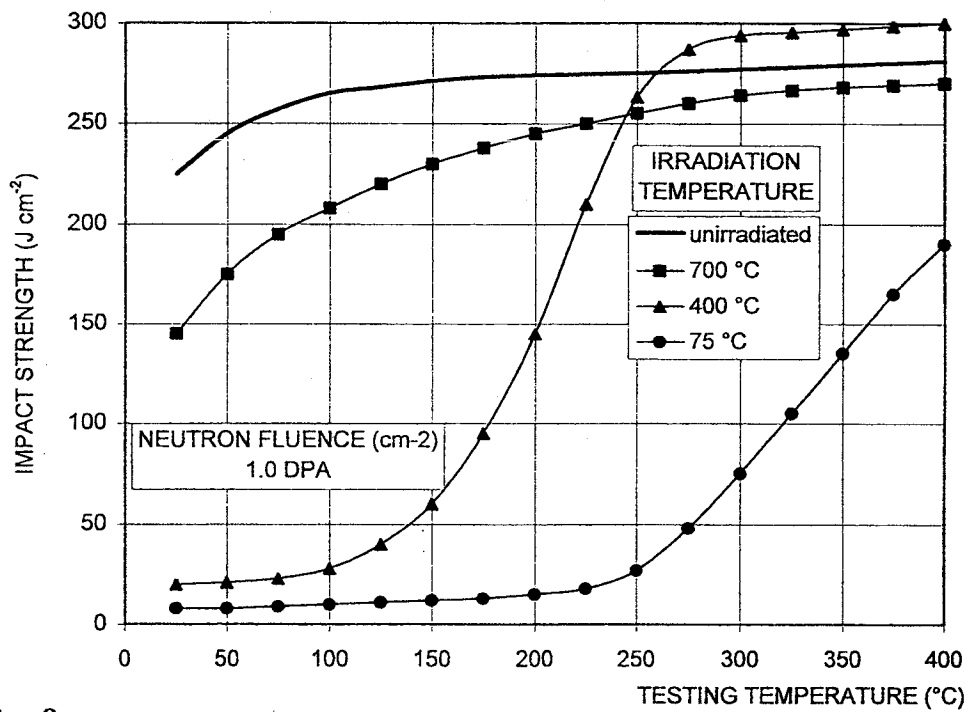
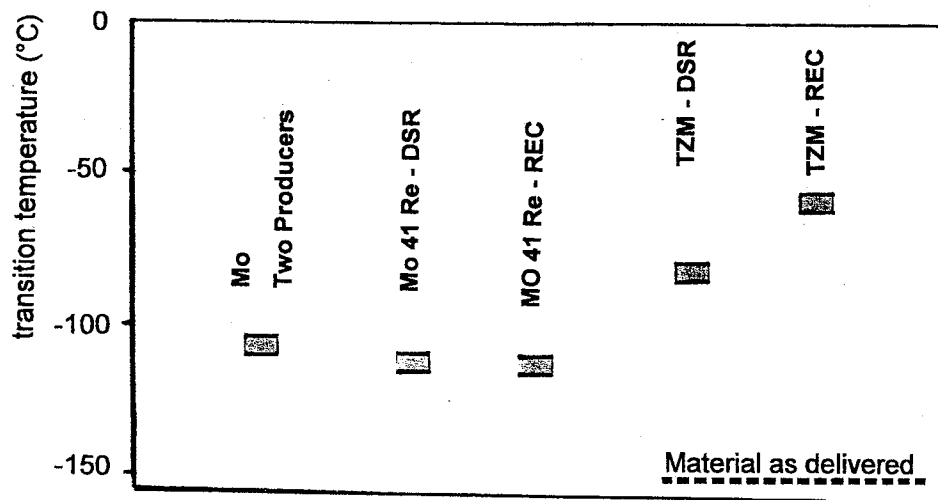
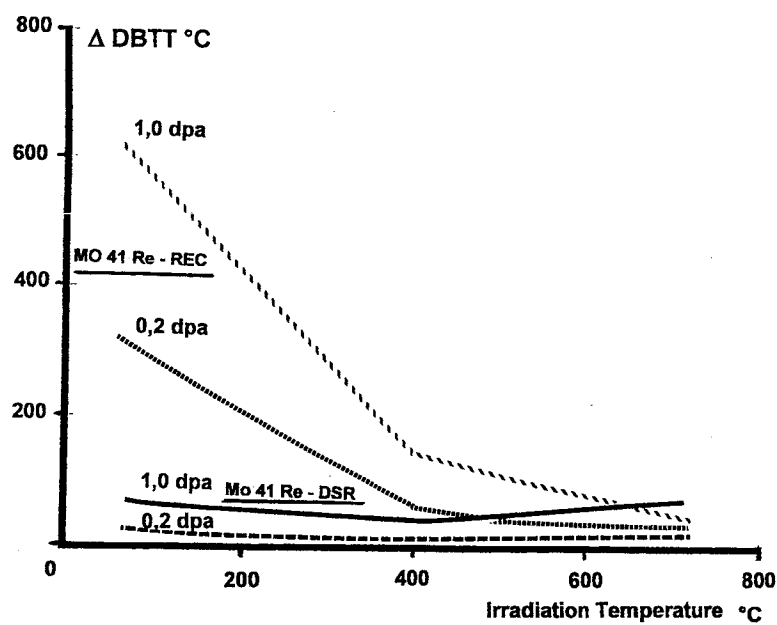


Fig.:8
Influence of Neutron Irradiation on the impact strength of Mo-41 Re (DSR)



Ductile to brittle transition temperature of Mo and Mo alloys measured by 3 point bending test



Difference of ductile/brittle transition temperature (Δ DBTT) measured by 3 point bending tests before and after neutron irradiation

Fig.:9 RESULTS FROM 3 POINT BENDING TESTS

Material	Mo			Mo-41Re			TZM	
	DSR	Z6	DSR	DSR	REC	REC	DSR	REC
As delivered	-115	-120*	-120*	-120*	-120*	-120*	-80	-65
Irradiated 0,30 dpa	95	115	20	20	320	320	70	125
75 °C 0,85 dpa	105	65	60	60	610	610	50	85
Irradiated 0,20 dpa	95	120	0	0	20	20	165	170
400 °C 1,10 dpa	785	820	20	20	150	150	480	?
Irradiated 0,17 dpa	105	95	0	0	20	20	105	175
700 °C 0,95 dpa	155	110	80	80	0	0	280	45

Ductile to brittle transition temperature (Δ DBTT) of Mo and Mo alloys, measured by 3 point bending tests before and after neutron irradiation (0C)

Fig.: 10

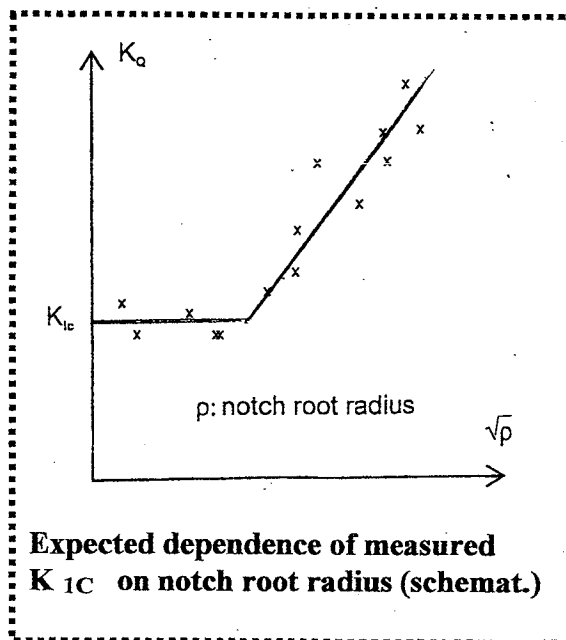
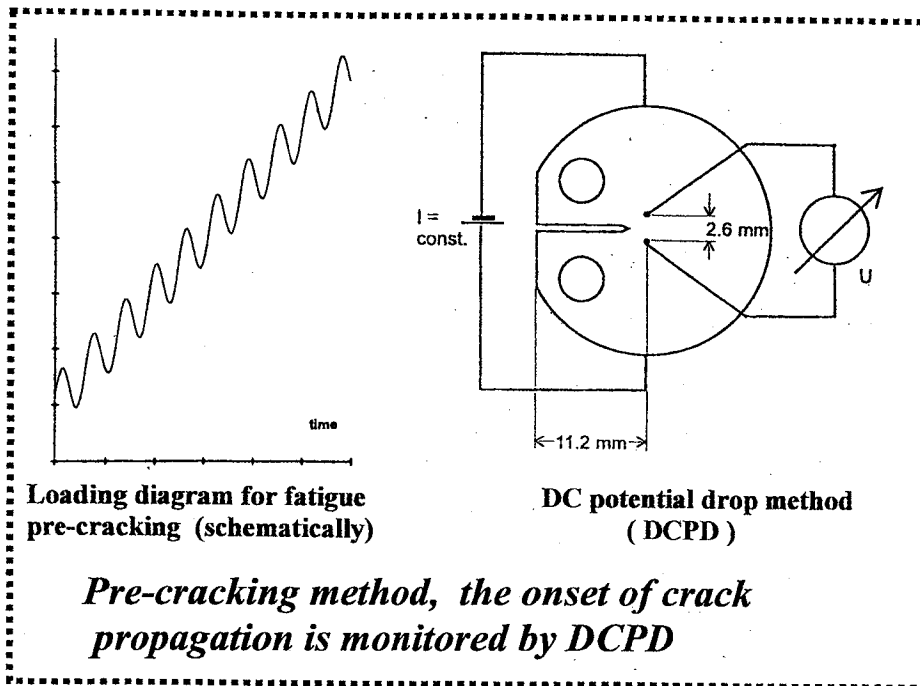
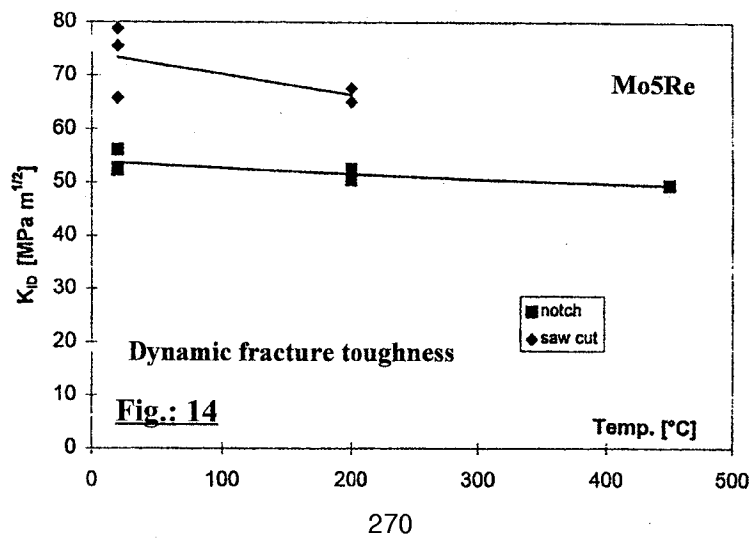
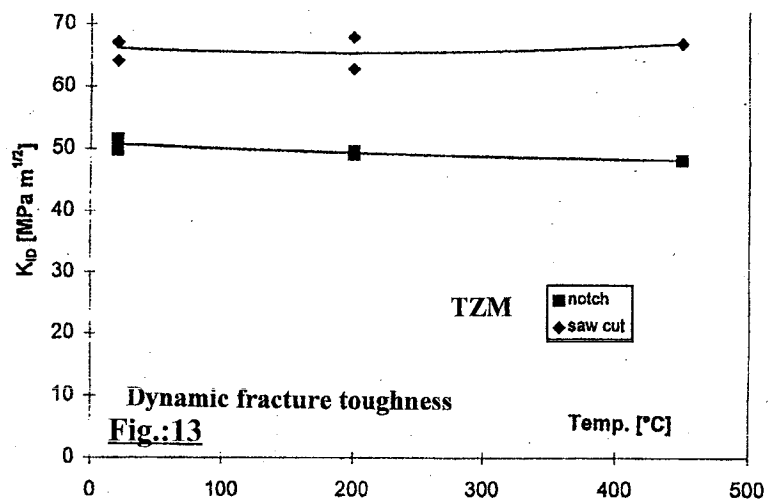
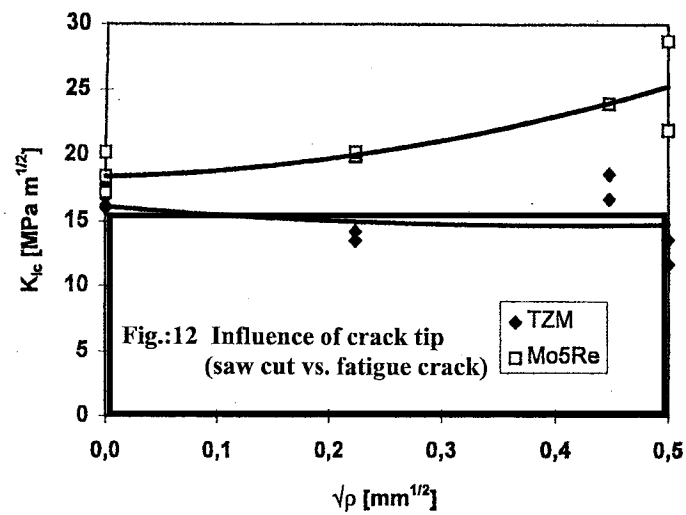
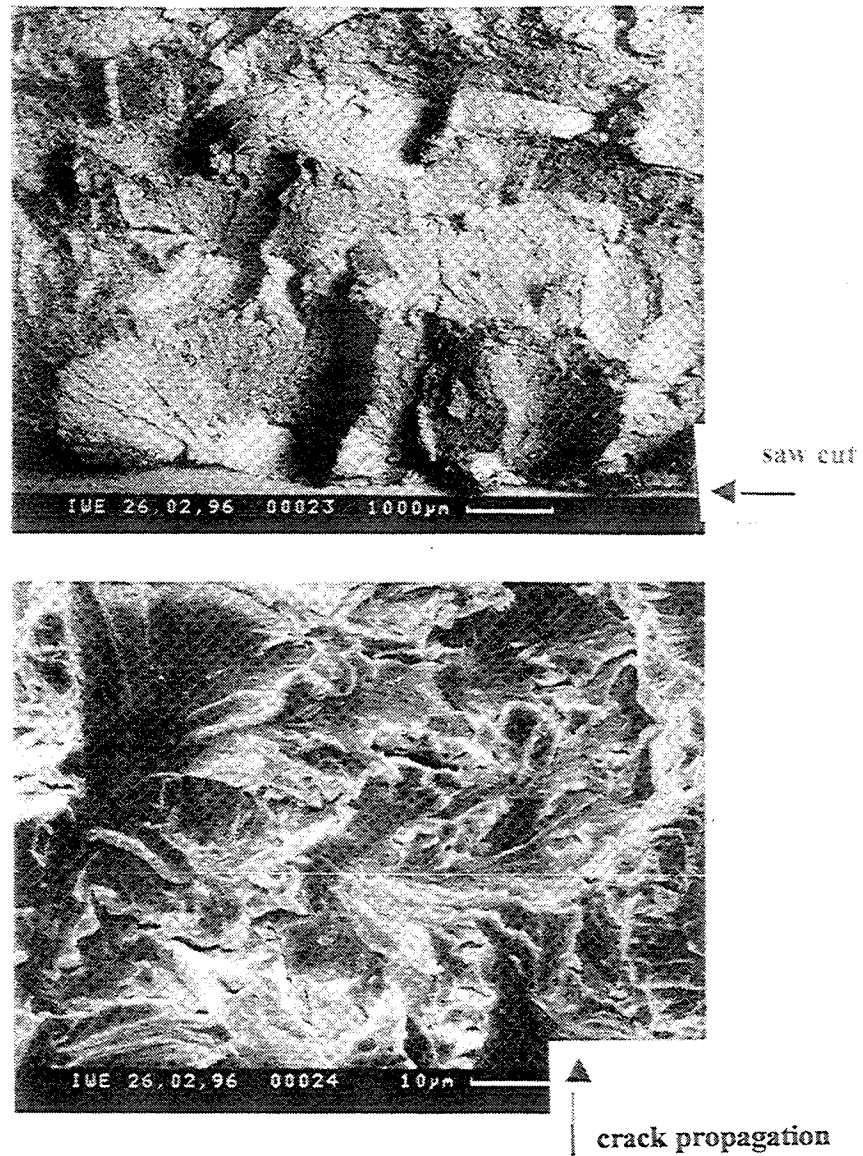
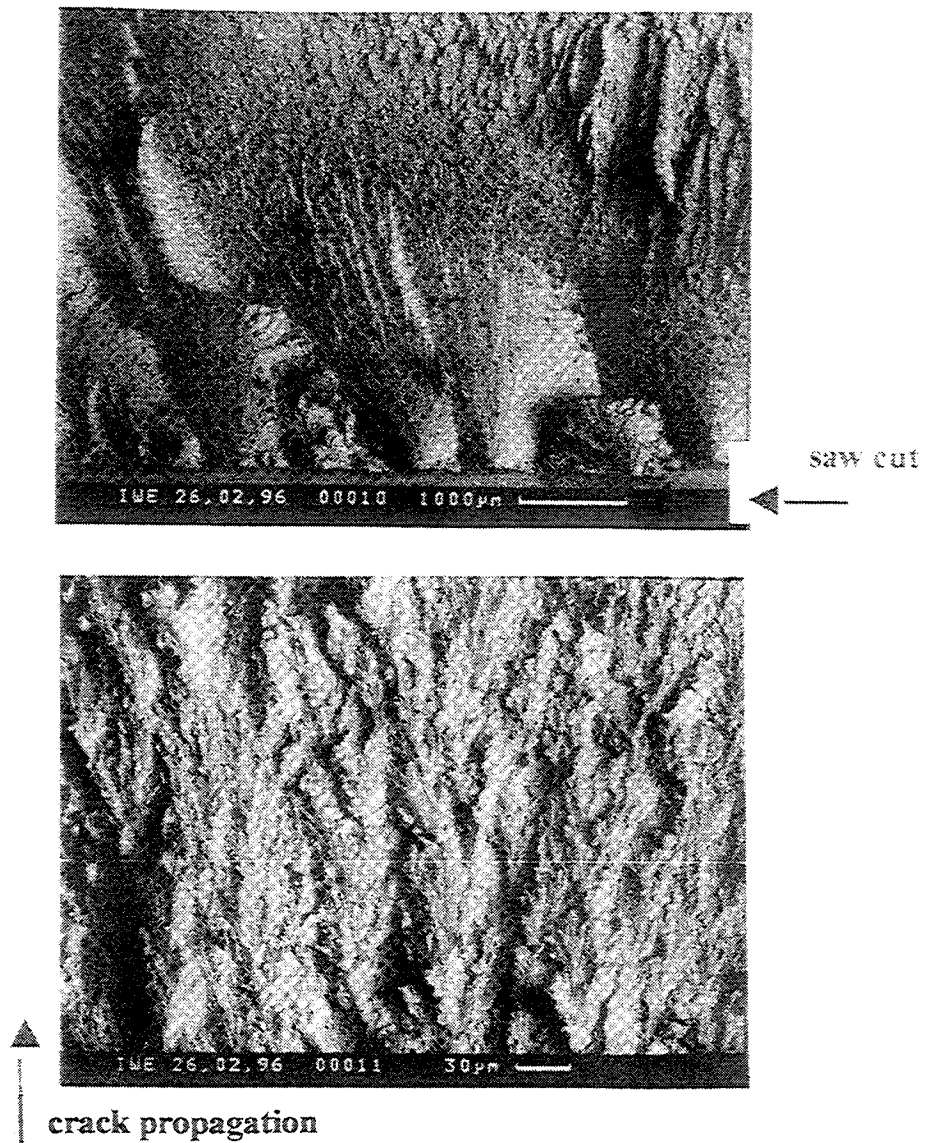


Fig:11





**SEM PICTURES OF FRACTURE SURFACE
FOR SAMPLE MA4 (Mo 5Re) Fig.:15**



**SEM PICTURE OF FRACTURE SURFACE NEAR
CRACK TIP FOR SAMPLE TA2 (TZM)**

Fig.:16

Materials Selection for Power Generation Applications (Gas Turbine Blades)

**Drs. Hanadi Salem, Amal Esawi, and Mahmoud Farag
Mechanical Engineering Department
The American University in Cairo**

Abstract

The relatively high fuel efficiency and lower initial installed cost of advanced combustion turbines have made them an increasingly important source of power generation. Of all the turbine parts, the blades are subjected to the most severe conditions and although good resistance to creep deformation and rupture has often been the prime requirement, achievement of creep strength alone does not present the major problem. The greatest difficulty is avoidance of undue deterioration in other material properties as creep resistance is improved. Toughness, oxidation and hot corrosion resistance, as well as processability usually suffer when alloying elements are added to improve creep strength.

Nickel-based superalloys have been the standard materials for turbine blades since the 50s for their good resistance to corrosion, mechanical and thermal fatigue, mechanical and thermal shock, creep, and erosion. Most superalloys have a maximum service temperature $<1000^{\circ}\text{C}$ in load-bearing applications. However, the introduction of directional solidification (DS) and single crystal (SX) technologies as well as internal cooling of the blades and thermal barrier coatings (TBC) allowed for peak operating temperatures of 1100°C in some turbines with service lives around 10,000 hours. Advanced gas turbine systems (AGTS) are expected to have turbine inlet temperatures (TIT) ranging between $1200\text{--}1400^{\circ}\text{C}$, which is much higher than the permissible level for superalloys. Currently, there are several materials systems under development, which could lead to higher operating temperatures and lighter weights of gas turbines for AGTS. Among these are intermetallic, monolithic ceramic, metal matrix and ceramic matrix composite materials. Accordingly, in the current work, selection and substitution analysis for the standard materials used for turbine blades as well as the new trend materials currently under investigation was conducted. It was perceived that monolithic ceramic SiC and SiC/SiC composites have the best potential for extensive use in turbine blade applications.

Keywords: Advanced gas turbine systems, turbine blades, design considerations, standard and new trend materials, material selection and substitution.

1. Introduction

The relatively high fuel efficiency and lower initial installed cost of advanced combustion turbines have made them an increasingly important source of power generation. Relatively high operating temperatures in the various stages of the turbine are among the main reasons for their superior thermal efficiency. Of all the turbine parts, the blades are subjected to the most severe conditions and the development of better materials for their manufacture has always been a challenge to the materials engineer. During the last 50 years, the turbine inlet temperatures have doubled as a result of developments in turbine blade materials and design.

A turbine blade material must satisfy several criteria in order to perform well in the severe environment in which it operates. Although good resistance to creep deformation and rupture has often been the prime requirement, achievement of creep strength alone does not present the major problem. The greatest difficulty is avoidance of undue deterioration in other properties of the material as creep resistance is improved. Toughness, oxidation and hot corrosion resistance, as well as processability usually suffer when alloying elements are added to improve creep strength. With the introduction of better blade materials, coatings to resist oxidation and hot corrosion, and blade cooling, modern combustion turbines operate at temperatures in the range of over 1100°C with service lives of 10,000 hours.

With the increasing trend to tie the power generated to the demand on energy and with the higher fraction of power generated from the less predictable renewable energy sources, fossil fuel fired power plants are facing increasingly larger load fluctuation, with the resulting component and materials problems. One of the most vulnerable sections of gas turbine blades is the trailing edge where the blade is thin.

This paper starts with a discussion of the design considerations in selecting materials for power generation applications, with special emphasis on turbine blades. After a review of the current materials, the new challenges facing components and materials are discussed. Finally, possible trends in gas turbine materials are explored.

2. Design Considerations

Plastic instability at elevated temperature, deformation mechanisms and strain associated with creep, stress and temperature dependence, fracture at elevated temperature, and environmental effects are among the issues that are usually considered when designing a component or a material for high temperature applications [1].

Creep: The main functional requirement of turbine blade materials is creep behavior, which covers creep resistance, stress rupture strength, and stress rupture ductility. While excessive creep strain can cause rubbing with stationary parts, stress rupture ductility is important in avoiding failure when the material cannot accommodate even the allowable small amount of creep deformation. Also creep rupture stress for the expected blade life should be more than the stresses encountered in service so as to avoid blade failure. Unfortunately, creep resistance is often obtained only with some sacrifice of ductility so that only a compromise is usually possible.

Thermal Stability: Stability of the microstructure and properties can be one of the more difficult requirements to guarantee. Grain growth, coarsening of phases and spheroidisation are among the changes that can cause deterioration of properties after long exposure to high temperature. Here again, structural stability is often obtained only with some sacrifice of ductility. Overaging of gamma prime precipitates in Ni-base superalloys is one of the serious

problems encountered due to elevated temperatures service conditions, which causes strength deterioration of the material. In addition, changes in the microstructure of superalloys at the operating temperature cause component embrittlement by the formation of brittle phases and continuous carbide phase formation along the grain boundaries.

Environmental Effects: *High temperature oxidation:* Occurs when a Ni-oxide layer is formed on the surface of Ni-superalloys temperatures greater than 538°C. This oxide layer tends to crack and spall when the blades are subjected to vibration and thermal cycling (startup/shutdown) during the engine operation. *Sulphidation:* Occurs when sulfur contained in the fuel reacts with oxygen and attacks the base metal. This issue becomes critical when sulphidation takes place at the blade root region, along the leading or trailing edges or under the blade shroud. *Hot Corrosion:* Occurs when combined oxidation-sulphidation attacks the blade hottest sections. *Standby-Corrosion:* Occurs during the turbine shut down as a result of air moisture and corrosive residuals staying long enough in contact with the blades and vanes surfaces. This significantly affects the blades' fatigue strength, and hence reduces their service lives.

Resistance to oxidation and high temperature corrosion are also important functional requirements for turbine blade materials. Sacrifice of corrosion and oxidation resistance is usually part of the compromise necessary to achieve high creep strength. An added difficulty is that the presence of gases such as oxygen, hydrogen, nitrogen, chlorine, and carbon dioxide can reduce creep-rupture strength and ductility. Oxygen diffuses along grain boundaries causing embrittlement. Sulfur can also penetrate grain boundaries leading to rapid crack propagation at high temperatures. The addition of grain-boundary modifiers, such as boron, or coating reduces these effects [1].

Erosion is another environmental effect, which is better resisted by harder materials. Erosion resistance of turbine blades can be improved by applying hard facing coatings. Erosion results from particles ranging between 5-10 μm suspended in the hot gases. It also occurs as a result of either spalling of the thermal barrier coating layer (inefficient bonding, low reliability, exceeding service life), or the oxidized layer formed on the blade surface as a result of thermal cycling and components' vibration. This is a typical problem encountered by the first stage blades and vanes subjected to highest turbine inlet temperatures.

Thermal Fatigue: Transient thermal gradients within a component can induce plastic strains, and the cyclic strain resulting from repeatedly applied gradients can cause component failure due to thermal fatigue. The effects of start-up and cool-down often can account for more reduction in life expectancy than creep. Thermal fatigue cracks initiate along the surface and progress inwards either inter-granularly or trans-granularly. One way to reduce thermal fatigue is to reduce section size.

Thermo-mechanical Fatigue: Results from the combined effect of fluctuating loads and temperatures. In the leading edge of gas turbine blades the maximum mechanical strain and lowest cycle temperature coincide, which is the condition for out-of-phase thermo-mechanical fatigue [2]. This problem is important in the case of coated blades, where Young's modulus, thermal expansion, and inelastic deformation behavior of the coatings are highly dependent upon the temperature and are often different from the respective properties of the substrate.

Thermal shocks: Conditions that lead to rapid changes in operating temperature can lead to appreciable differences between the temperature of the outer surface regions and that of the inner core of the blade. This results in strains, which if locally greater than the ductility of the material, the blade will crack in that region. Thermal shock resistance of the blade material

deteriorates as its thermal conductivity and ductility decrease and as its thermal expansion coefficient and elastic modulus increase.

Toughness: Toughness is important since blades must withstand impact loading from foreign solids that may get into the system. In many cases, creep resistance and thermal stability are obtained at the expense of ductility so that only a compromise is usually possible.

Weight: Weight becomes an important element in materials selection in aerospace applications. Weight also contributes to the stresses acting on the blade as a result of the centrifugal forces. This factor can be taken into account by comparing materials on the basis of specific strength (strength/specific gravity).

Processability: This material property depends on the intended means of shaping the blade. Hot working, casting, and powder metallurgy are the main processing methods. Wrought alloys should exhibit sufficient ductility at the working temperature, while cast alloys should be free from porosity and segregation. The presence of complex internal cooling channels represents an additional challenge to the production engineer.

Cost: The major installed cost elements of a turbine blade include material, processing, coating, and inspection. Length of service and repair costs should be included when making selection decisions on the basis of life-cycle cost.

3. Current Blade Materials

Superalloys

Nickel-based superalloys have been the standard materials for turbine blades since the 50s. Superalloys, generally, have good resistance to corrosion, to mechanical and thermal fatigue, to mechanical and thermal shock, to creep and to erosion at high temperatures. Most superalloys have a maximum service temperature of 1000°C in load-bearing applications.

Properties of superalloys have continually improved over the years by adding various alloying elements and by strengthening techniques. The turbine blades of the Whittle gas turbine (c. 1940) were made of a simple Ni-Cr alloy. This material presented some limitations in terms of high temperature strength and oxidation resistance. Efforts to improve the high temperature strength focused on increasing the content and controlling the distribution of the intermetallic γ' (Ni_3Al , Ti , Ta , Nb); solid-solution hardening by including cobalt, molybdenum and tungsten; and introducing carbide formers, tantalum, niobium and hafnium [3]. Oxidation resistance was improved by adding more chromium (e.g. IN-738 and IN-939) which forms an oxide layer of Cr_2O_3 that protects the blade from attack by oxygen.

Superalloys are very hard materials that cannot be machined easily. Since the 50s, blades were produced by investment casting and special cast alloys were developed specifically for that process. The development of powder techniques in the 60s (the driving force being the incorporation of cooling channels in the blades) also led to the development of special powder alloys (e.g. Nimonic alloys 90, 100 and 105) from which blades were made. In the 1970s, more alloys (e.g. MA 6000E alloy) became available as a result of developments in *mechanical alloying*. This is achieved using a high energy milling process in which powders (both metallic and non-metallic) are repeatedly fractured to expose clean surfaces and then subsequently welded together.

Many alloys have been used as blade materials and Table (1) gives some examples:

Table (1) Traditional Materials and Their Properties

	Max. Temp. °C	Thermal Stability	Thermal Conductivity (W/m-K)	Thermal Expansion Coefficient ($\times 10^{-6}/^{\circ}\text{C}$)	Thermal shock/fatigue	Toughness K_{IC} ($\text{MN}/\text{m}^{3/2}$)	Density (g/cm^3)	Cost (\$)
IN 713	970	3	10.9	10.6	1.03	100	7.91	30
IN 100	1000	3	12	13	0.92	100	7.75	30
MAR-M-200 (DS)	920	3	13.5	10	1.35	120	8.53	50
M 247 (DS)	1035	3.5	12	10	1.2	100	8.95	50
PWA 1484 (SX)	1095	3.5	12	10	1.2	100	8.5	60
CMSX10 (SX)	1125	4	12	10	1.2	100	9.05	60

Although research efforts have resulted in the development of several generations of superalloys, practical temperatures for those alloys (including blade cooling) only reached $<1100^{\circ}\text{C}$. Since 1985, there have been no major breakthroughs in the development of nickel-based superalloys. Their future potential is limited. Further turbine inlet gas temperature increases became possible with the introduction of DS and SX technologies, which continued to push up the practical temperature limits.

Directionally Solidified Blades

Because the presence of grain boundaries makes the blade alloys susceptible to creep and cracking under the high operating temperatures and centrifugal forces involved, DS and SX techniques were developed. In DS, grains are aligned longitudinally with no transverse grain boundaries, which makes the blades stronger in the direction of the applied stress. This meant failure by void formation, as is the case with polycrystalline metals, was eliminated. As a result DS blades allowed turbine operating temperatures to increase by 25°C more than conventional blades [4].

Single Crystal Blades

Single crystals are made by a special technique in which crystals are grown in a mould which has a constriction in the shape of a corkscrew or helix; the cross section of which is so small that it allows only one crystal to grow. Single crystal blades are more expensive than either conventional or DS ones, however the lack of grain boundaries makes the blades resistant to creep and thermal shock so they have a longer and more reliable service life. As a result they allow a further 25°C in blade operating temperatures [4, 5].

4. Blade Cooling and Thermal Barrier Coatings

Blade Cooling

Progress in materials has proceeded concurrently with developments in the design of blades, manufacturing and surface coatings. Since the 40s, gas inlet temperatures higher than the melting point of the blade material (nickel-base superalloys) became possible. This was achieved by introducing internal cooling of the blades.

At its introduction, *internal cooling* (passing cold air through cooling channels along the full length of the blade) allowed the inlet temperature to be increased by 100°C without changing the alloy composition [4,10,11]. Later *film cooling*, in which air is passed over the surface through little holes giving a cool boundary layer between blade and gases, was introduced. Developments in blade cooling have become quite sophisticated over the years and have allowed more increases in inlet temperature. However, ducting cold air through the blades reduces the thermal efficiency by taking too much of the heat away from the combustion chamber. Accordingly, by these impeding limits to the internal cooling of turbine blades emphasis has switched back to materials development [11,12].

Thermal Barrier Coatings

Thermal barrier coatings (TBC) used extensively in aircraft turbines allow for another 100°C increase in operating temperatures. Currently the peak metal temperatures of over 1,100°C are experienced in some turbines with service lives around 10,000 hours.

Important steps are being taken to optimize coatings for superalloys single crystal turbine blades for AGTS. Turbine inlet temperatures in advanced turbines could exceed 1,400°C, which requires components capable of withstanding high temperatures and pressures with improved coating durability greater than 30,000 hours. Currently used TBCs are susceptible to phase degradation, creep at temperatures over 1,200°C, which result in degraded compliance and insulation efficiency [12]. TBCs currently in use are based on Yttria stabilized zirconia (YSZ) with durability less than 10,000 hours. Surface deposits, such as glassy dust and sulfate salts can penetrate the porous TBCs and damage their strain-tolerant microstructure, resulting in premature chipping or flaking. A team at the University of Pittsburgh has studied two TBC systems [13]. The first of which is a bond coat composed of platinum aluminide (PtAl), and the second has a nickel-cobalt-chromium-aluminum-yttrium bond coat prepared by argon-plasma-spraying. In rapid cyclic heating from 1,100°C to 30°C six times per hour, the spalling time recorded for the PtAl system was about 500 hours, while a 700 hours of spalling time was recorded for the NiCoCrAlY. Further coatings research is aimed at improving the stability of the bond coatings and reliability of TBCs. Those produced by plasma spraying are not suitable for rotating parts; conversely, TBCs made by electron beam physical vapor deposition (EB-PVD) have been successfully applied to rotating components. TBC systems with a 1,300°C with capability for a minimum of 5,000 hours are to be achieved by December 2002. Other coatings are also developed for increasing the resistance against particle erosion through blade tip hard-facing. In this process, hard particles about 100-150 µm are brazed onto the blade tip along the chord of the very thin profile [14].

The following section will deal with the recent advances in materials and processing that could be suitable candidates for AGTS and that are capable of withstanding operating temperatures > 1100°C. Advanced materials for AGTS can be classified into three categories: (1) TBC for currently used Ni-superalloys, (2) monolithic ceramic and intermetallic blades, and (3) Fiber reinforced composites, such as metal matrix composites (MMC), and ceramic matrix composites (CMC).

5. Recent Trends in Turbine Blade Materials

The demand for the development of AGTS running on varieties of fuels, such as clean natural gas as well as fuels such as coal led several agencies to concentrate their efforts on the development of the materials necessary to withstand the expected high operating temperatures and the harsh corrosive effect of the hot gases. Among these recent R&D programs sponsored by The Department of Energy (DOE): Framatome and CEA, The Foundation For Innovative Systems (FIS), Advanced Technology Program (ATP), Version 21, Advanced Turbine

Technology Application Project (ATTAP), Advanced Gas Turbine Project (AGT), Advanced Ceramic Engine Technology for Gas Turbines (ACETGT). Other programs Such as: The National Lucht-en Ruimtevaartlaboratorium (NLR), Netherlands Agency for Aerospace Programs (NIVR), and The Status of Gas Turbine Programs in Japan (CGT) [15] are also working on the development of materials for advanced-efficient power generation systems. Table (2) gives some examples of some of the experimental turbine blade materials that are under development.

Table (2) Examples of Experimental Turbine Blade Materials

	Max. Temp °C	Thermal Stability	Thermal Conductivity (W/m-K)	Thermal Expansion Coefficient ($\times 10^{-6}/^{\circ}\text{C}$)	Thermal shock/fatigue	Toughness K_{IC} ($\text{MN/m}^{3/2}$)	Density (g/cm^3)	Cost (\$)
Intermetallic TiAl	750	3	10	10	1	40	3.9	40
Monolithic Ceramic SiC	1400	5	93	4.8	19.38	3.5	3.2	50
Monolithic Ceramic Si_3N_4	1400	5	33	3.65	9.041	5	3.1	50
Monolithic Ceramic Al_2O_3	1460	5	34	6.5	5.23	4.2	3.98	50
MMC (Ti-SiC)	800	1	6.5	7.9	0.82	30	2.82	80
MMC (Ni-SiC)	1150	3.5	6.5	10	0.65	30	3.5	80
CMC (Si_3N_4 -30%SiC)	1500	4	40	5.5	7.27	10	3.2	70
CMC (Al_2O_3 -30%SiC)	1640	3.5	22	5.2	4.23	9	3.75	70
SiC/SiC	1400	4	93	4.8	19.38	22.7	3.2	70

Monolithic Ceramic blades

Silicon carbide (SiC) and silicon nitride (Si_3N_4) families of ceramics are considered for turbine blades because of their better thermal shock resistance due to their low thermal coefficient of expansion, high strength, and moderate thermal conductivity. Si_3N_4 material is capable of retaining room temperature strength of 140 MPa up to operating temperatures of 1400°C. These materials can be fabricated to near-net shape either by reaction-bonding or hot-pressing techniques at costs competitive with the forged, DS or SX turbine blades [16]. A major drawback of silicon carbide and nitride components is their sensitivity to macroscopic flaws that are bigger than 150 μm . Solution of this problem required the development of processing techniques that could achieve additional densification of the sintered part, such as Hot Isostatic Pressing (HIP). During 1990s research was directed towards improving the fracture toughness of the sintered Si-carbide and nitride blades through minimizing the flaw size and microstructural refinement. Improving fracture toughness of such materials is essential since fracture of a ceramic part in a turbine could likely lead to fracture of the adjacent parts and hence complete engine failure. Ceramic materials are strong competitors to conventional turbine blades and vanes as they allow operating temperatures up to about 1370°C with un-cooled configurations [17-20].

Monolithic Intermetallic Blades (TiAl)

A growing interest has been taking place for intermetallic materials such as TiAl or Ti_3Al due to their low density and enhanced temperature capability compared to conventional Ti-alloys.

TiAl parts are usually manufactured by investment casting. Their specific strength is superior to Ni-base superalloys. In USA, TiAl-blades and vanes have been successfully tested in engines, however, more testing is still necessary before commercializing. On the other hand, Ti_3Al , which is normally processed by forging, has limited interest due to its high density and complicated processing [21].

Metal Matrix Composites (MMC)

High strength Ti-based MMCs are the most suitable candidate for turbine blades. They offer a potential for weight reduction up to 50% relative to conventional Ti-alloys. High modulus-continuous fibers of SiC about 0.1 mm in diameter are used for the reinforcement of the Ti-matrix [10]. The SiC fibers are coated with carbon layer in order to prevent extensive reactions between the fiber and the matrix during the final processing step. Fibers are coated with the Ti-matrix using plasma or PVD. HIP is used for the final consolidation.

Another type of MMCs belongs to a class called *eutectics*, in which a spontaneously aligned reinforced structure is formed when directionally solidified. Examples of these composites are Ni-MMCs with TaC reinforcing fibers, Co-MMCs with TaC reinforcing fibers, Ni_3Al -MMC with Ni_3Nb reinforcing plates, Co-MMCs with Cr_7C_3 reinforcing fibers, and Nb-MMCs with Nb_2C reinforcing fibers. The high melting point fibers and the atomic bonding between the fibers and the matrix greatly improve the creep properties and strength of the composite alloy [22]. As a result, DS eutectics can increase the inlet temperature by 100°C above DS nickel alloys. Improvements in composite alloy design can allow even higher temperature increases. [4]

Ceramic Matrix Composites (CMC)

The low density and high temperature strength of ceramics made them attractive materials for gas turbines. As was discussed earlier, the low service fracture toughness of monolithic ceramic components is their major drawback for engine-applications. However, fiber reinforced CMCs could offer a solution for this problem. Accordingly, lots of R&D efforts are currently conducted through the various agencies in order to improve the properties of CMC by fiber reinforcement. SiC, and Al_2O_3 are examples of reinforcing fibers in a matrix of either SiC, Al_2O_3 or a mixture of both [22]. One of the disadvantages of non-oxide fiber-reinforced ceramics is their potential for chemical reaction between the fibers and the matrix at operating temperatures >1000°C for several hundred hours. In addition, the oxide fiber-reinforced composites could suffer from their creep property deterioration with time [23]. The NASA's Glenn Research Center in Cleveland investigated the ceramic composites in rocket engine turbines to increase safety and reduce cost. A turbine bladed disk (blisk), made out of carbon fiber reinforced SiC matrix can withstand temperatures about 1,100°C. The increased turbine efficiency allows for heavier payloads. Moreover, since the composite blisk is only about ¼ the weight of the metal disc, the weight saved can be used to increase the weight of the payload for aerospace applications [22].

6. Materials Selection for Gas Turbine Blades

Generally, the material selection process starts with an analysis of the material performance requirements, which includes:

- Functional requirements.
- Resistance to service environment.
- Processability requirements.
- Cost.

In the case of gas turbine blades, functional requirements include resistance to creep and rupture, toughness, thermal stability, density, and resistance to thermal shock and fatigue. While these properties are readily available for established materials under various service conditions, they are not easy to find for new and experimental materials, which makes selection and substitution decisions difficult. In the present analysis, material properties are graded on a five-point scale of excellent (5), very good (4), good (3), fair (2), and poor (1).

Resistance to service environment includes oxidation, corrosion, and abrasion. This factor will not be included in the present analysis as appropriate coatings can now be used to protect most materials. The method of processing a given material is influenced by whether it is available as wrought, cast, or powder and by whether cooling channels are needed. To simplify the present analysis, processability will be included as part of the cost. Therefore, the cost in this case is considered as the installed cost, which includes material, processing, coating, and inspection. A more accurate comparison of the cost would take into account the length of service and repair costs, which is the life-cycle cost. In this analysis, materials are compared on the basis of an estimate of the installed cost and a five-point scale is used for comparison, with the least expensive being 5 and the most expensive being 1, see Tables (1) and (2).

To compare materials, the weighted properties procedure outlined in [24] was followed. The first step was to use the digital logic method in estimating the relative importance (weighting factors) of the different material properties for a given application. This was done for the two following applications:

- Engines for missile and aerospace applications with the main requirements of high maximum power, reliability, and lightweight. Relatively shorter lifetime can be tolerated.
- Engines for auxiliary power units with the main requirements of long life, tolerance to changeable loading, and reliability. Engine weight is not an issue.

Table (3) gives the weighting factors that were obtained using the digital logic method.

Property	Maximum temperature	Thermal stability	Thermal fatigue/shock	Toughness	Density	Cost
Relative importance in missile and aerospace engines	0.24	0.08	0.16	0.18	0.26	0.08
Relative importance in engines for auxiliary power units	0.14	0.26	0.20	0.16	0.06	0.18

Comparison Among Traditional Materials:

According to the weighted properties procedure the first step in comparing materials is to normalize the properties so that the best value for a given property gets 100 and other values are related to it. Table (4) gives the normalized properties of the traditional materials in Table (1). The performance index (γ) for the different traditional materials is then calculated as the total sum of (normalized property * its weighting factor). Table (5) gives the performance index values for the applications in missile and aerospace and auxiliary power generation. The performance index values of Table (5) show that MAR-M-200 (DS) has the highest value with CMSX10 (SX) being a close second.

Table (4) Normalized Properties of Traditional Materials

	max. temp.	thermal stability	thermal shock	toughness	density	Cost
IN 713	86.22	75	76.17	83.3	97.98	100
IN 100	88.89	75	68.39	83.3	100	100
MAR-M-200 (DS)	81.78	75	100	100	90.86	60
M 247 (DS)	92	87.5	88.89	83.3	86.59	60
PWA 1484 (SX)	97.3	87.5	88.89	83.3	91.18	50
CMSX10 (SX)	100	100	88.89	83.3	85.64	50

Table (5) Performance Index of Traditional Materials

	Performance Index in Auxiliary Power Generation	Performance Index in Missile and Aerospace Applications
IN 713	84.02	87.36
IN 100	82.96	87.27
MAR-M-200 (DS)	86.45	89.05
M 247 (DS)	82.74	85.62
PWA 1484 (SX)	82.00	87.29
CMSX10 (SX)	85.25	87.49

Selection from Traditional and Experimental Materials:

The process of selection is repeated for the combined list of materials in Tables (1) and (2) and the resulting performance index values are given in Table (5). The performance index values of Table (6) show that the monolithic ceramic SiC and SiC/SiC composite perform equally well and have the highest values for applications in missile and aerospace applications. In auxiliary power generation applications, however, the monolithic ceramic SiC has a clear advantage over other materials.

Table (6) Performance Index of Traditional and Experimental Materials

	Performance Index for Auxiliary Power Generation	Performance Index for Missile and Aerospace Applications
IN 713	52.57	53.03
IN 100	58.82	53.60
MAR-M-200 (DS)	53.83	51.63
M 247 (DS)	54.49	50.54
PWA 1484 (SX)	53.31	51.10
CMSX10 (SX)	56.03	51.76
Intermetallic TiAl	46.64	49.27
Monolithic Ceramic SiC	75.03	75.00
Monolithic Ceramic Si ₃ N ₄	64.75	67.50
Monolithic Ceramic Al ₂ O ₃	59.9	59.37
MMC (Ti-SiC)	30.22	50.07
MMC (Ni-SiC)	44.75	53.49
CMC (Si ₃ N ₄ -30%SiC)	56.00	64.47
CMC (Al ₂ O ₃ -30%SiC)	50.44	59.36
CMC (SiC/SiC)	69.30	74.91

7. Conclusions

The present analysis gives a methodical way of selecting a material for a given application. The results of the analysis depend on the weighting factors allocated to each property and on the accuracy of the values allocated to each material property. Allocating the weighting factors involves subjective judgment, even when the digital logic method is used. In the present case, sensitivity analysis has shown that the final results are not affected by small changes in weighting factors.

The major challenge to the accuracy of the present analysis comes from lack of accurate information about material properties, especially for thermal stability and thermal shock/fatigue. Another difficulty comes from the fact that the properties of experimental materials are unavailable and depend to a large extent on the method of preparation and quality of the raw materials involved in making them.

Finding the cost of making a turbine blade out of a specific material was also a challenge. Such cost depends on the number of blades produced, method of production, size of the blade, whether a thermal barrier coating is needed, and whether internal cooling channels are used.

In spite of the above difficulties and inaccuracies, it is felt that the present analysis gives an indication of the directions that those involved in developing new materials can pursue. Based on the present analysis, it is perceived that monolithic ceramic SiC and SiC/SiC composites have the best potential for extensive use in turbine blade applications.

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NEW DEVELOPMENTS OF THERMAL BARRIER COATING SYSTEMS FOR COMPONENTS IN GAS TURBINES

Robert Vaßen

Institut für Werkstoffe und Verfahren der Energietechnik (IWV1)

Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

ABSTRACT

Recent developments in the field of new thermal barrier coatings for gas turbine applications will be reviewed. In the first part, a selection of suitable ceramic candidate materials will be presented. These materials include oxides with pyrochlore, perovskite, garnet and also other structures. A comparison and discussion of the physical properties, especially thermal conductivity, thermal expansion and thermal stability, will be given.

In the second part, the performance of coatings from these materials will be described. Of special interest is the sintering behaviour and the results of thermal cycling tests. At present, the amount of published work on these application oriented issues is rather limited. Hence, our own work will be in the foreground in this section.

In the last part, new TBC concepts will be discussed. The concepts include nanophase materials and layered or graded structures. Results of our own concept with a two-layer TBC structure consisting of YSZ and pyrochlore materials will be given. At elevated surface temperatures beyond 1300 °C this concept leads to improved thermal cycling life times of at least a factor of 2 compared to the standard YSZ based system.

INTRODUCTION

Many different international research groups are recently developing thermal barrier coatings. This can be illustrated by the large number of review articles which exist on this topic. Some recent articles are listed in the references [1, 2, 3, 4, 5]. The number of articles is certainly also promoted by the high complexity of the subject. A TBC system includes in most cases the substrate, the so-called bond coat and finally the insulative – in most cases ceramic – top coat. All these components react with each other or the environment to a more or less extent and/or they undergo detrimental changes due to thermo-mechanical treatments during operation. The present paper will be focused on recent developments to improve the ceramic part of the TBC system.

The use of thermal barrier coating systems in gas turbines or diesel engines lead to improved performance. The insulative layer can provide a reduction of the temperature of the metallic substrate which results in an improved component durability. Alternatively, an increase of efficiency can be achieved by allowing an increase of the turbine inlet temperatures [6].

There are two major directions of development in the area of TBCs. First, it is tried to improve the insulative capability of the coatings by the reduction of the thermal conductivity. This can either be achieved by looking for new materials with a low thermal conductivity or by a modification of the microstructure of the coating. Details on both directions of development will be given in the present paper. A second important area of research is related to the improvement of the temperature capability of the TBC. The state-of-the-art coating for TBCs is nowadays 7 – 8 wt. % yttria stabilised zirconia (YSZ). This material has been identified during the last 2 and a half decades of extensive work on TBCs as a favourite material for this application, e.g. in the fundamental early work of Stecura [7]. However, the maximum surface

temperatures of these coatings is limited to about 1200 °C for long-term operation. The reason for this limitation will be discussed. Hence, an ideal new thermal barrier coating material should combine a reduced thermal conductivity and an enhanced temperature capability compared to YSZ while the other critical properties (thermal expansion coefficient, corrosion resistance, etc.) should be comparable to the properties of YSZ.

DEGRADATION OF YSZ DUE TO THE LIMITED HIGH TEMPERATURE CAPABILITY

At higher temperatures (> 1200 °C) the degradation of the YSZ top coat becomes increasingly important. One degradation mechanism of the standard YSZ is the accelerated phase transformation from the t'-phase to the equilibrium tetragonal and cubic (t + c) phases above 1200 C [8]. During cooling, the equilibrium tetragonal phase transforms to the monoclinic (m) phase, which is accompanied with a volume increase of about 4 %. This volume increase might result in a disintegration of the coating especially with increasing amounts of transformed t'-phase. Furthermore, enhanced sintering of the coating, i.e. the reduction of the porosity and an increase of Young's modulus [9] will take place at elevated temperatures. These changes of microstructure and mechanical properties will result in higher thermally induced stresses and a decrease in thermal fatigue life time of the coating [4]. Additionally, the sintering leads to an increase of the thermal conductivity and hence, to a reduced insulative protection of the substrate [10].

NEW CHEMICAL COMPOSITIONS

A selection of thermal barrier coating materials based on new chemical compositions will be given in this section. Certainly, the list of materials cannot be complete due to the fact that only part of the work is published.

In Germany several groups are working on TBCs based on a perovskite structure [11,12]. Of course, only a few compositions of this large materials class are of interest, especially those with high melting points (> 2000°C). In our institute especially two perovskites, namely BaZrO₃ and SrZrO₃, have been investigated. With respect to thermal expansion coefficient and thermal conductivity SrZrO₃ is comparable to YSZ, while BaZrO₃ is worse. However, it turned out, that both materials have relatively low thermal stability for a TBC application [12].

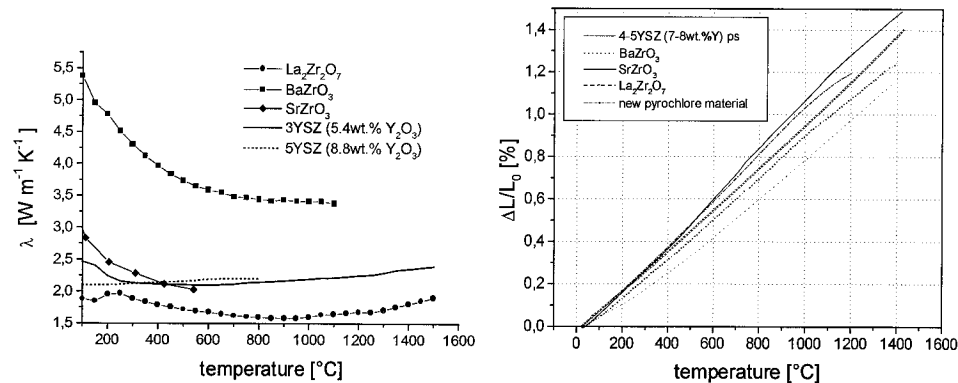


Fig. 1 Thermal conductivity (left) and thermal expansion (right) of new thermal barrier coating materials compared with standard YSZ.

Another very interesting candidates for new TBCs are materials with pyrochlore structure [13, 12]. Especially materials based on lanthanum zirconate, $\text{La}_2\text{Zr}_2\text{O}_7$, show favourable properties for this type of application, e.g. low thermal conductivity and high thermal expansion coefficients (Fig. 1). These materials can be further improved by doping with rare earth elements. The thermal stability has been demonstrated in annealing experiments up to 1400°C [14]. Thermal cycling tests of plasma-sprayed coatings revealed promising results even without optimisation of the coating.

Padture and Clemens measured thermal conductivity in garnets with respect to an application as thermal barrier coating [15]. They found high temperature values between 2.4 and 3.1 W/m/K for the investigated compositions. Garnets with a thermal conductivity clearly below that of YSZ (about 2.0-2.7 W/m/K for stabilised zirconia [15]) have not been found.

NANOSTRUCTURED MATERIALS

Recently, nanostructured materials have been suggested as candidates for thermal barrier coatings [16]. An interesting property of these materials is the possible reduction of thermal conductivity due to phonon scattering at grain boundaries. An about 30 % decrease was predicted in nanocrystalline 7 wt.% YSZ of 100 nm grain size in a theoretical work by Klemens and Gell [17]. However, experimental results show that a grain size of 30 nm and below is necessary to get a significant reduction in YSZ [18]. These results might be qualitatively understood by the high amount of oxygen vacancies in YSZ, which are effectively scattering phonons and hence, reducing thermal conductivity. A further reduction, e.g. by a high density of grain boundaries, seems to be difficult and only possible at very small grain sizes. A further problem is grain growth in nanocrystalline structures. Above 900 °C a stabilisation of the structure is required, e.g. by the use of composite structures like YSZ / Al_2O_3 or by using multilayer nanostructured ceramic TBCs [19]. Whether this concept is successful has to be demonstrated in the future.

MULTILAYERS AND GRADED COATINGS

Stresses in ceramic coatings on metals can effectively be reduced by the use of a graded interlayer between the metallic substrate and the ceramic layer [20]. This approach was also applied to thermal barrier coatings applying a graded coating between bond coat and top coat. However, due to the higher surface area of a graded bond coat compared to a step wise compositional change fast oxidation of the bond coat was observed [21].

Very promising are approaches which use graded or multilayer structures within the ceramic top coat. One possibility is the use of a two layer top coat, in which the ceramic layer in contact with the hot gases is especially resistant against corrosive or erosive attack [22]. Alternatively, it is possible to use newly developed ceramic materials with improved high temperature capability. Often these materials have a lower coefficient of thermal expansion (TEC) or a reduced mechanical strength and fracture toughness, which might lead to early failure in thermal cycling tests. Using a standard YSZ layer with a high TEC and good mechanical properties will reduce crack growth in the most critical region close to the bond coat. These so called double layer systems have been produced by APS using 8 wt.% YSZ and $\text{La}_2\text{Zr}_2\text{O}_7$ in our institute. In Fig. 2 a micrograph of such a coating after thermal cycling in one of our gas burner test facilities is shown. It could be shown that the performance of these systems at high surface temperatures (>1330°C) is by at least a factor of two better than the one of conventional single layer YSZ systems.

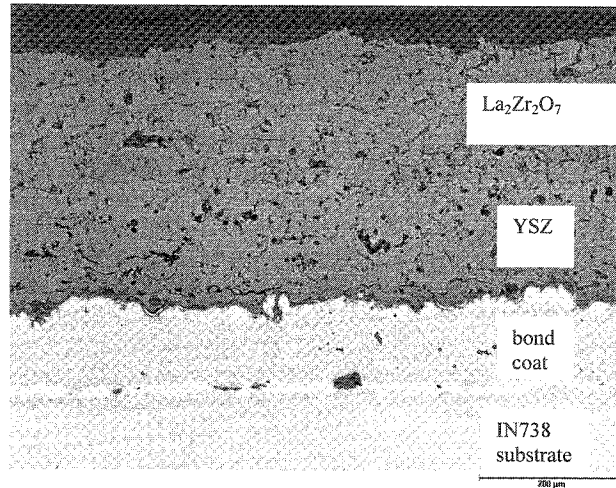


Fig. 2 SEM micrograph of a double layer thermal barrier coating consisting of YSZ and $\text{La}_2\text{Zr}_2\text{O}_7$ ceramic top coats.

SUMMARY

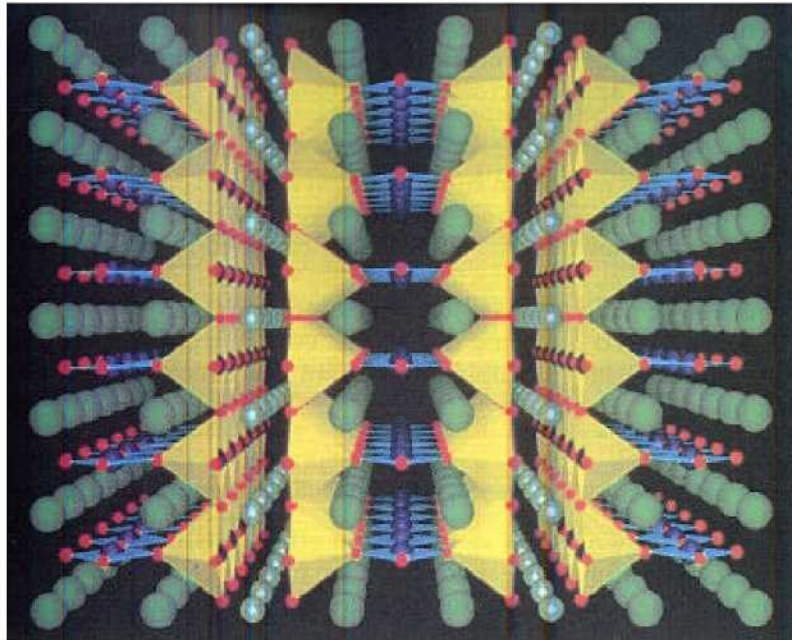
A description of conventional thermal barrier coating systems was given. Special emphasis was put on the limited high temperature capability of these systems. New concepts designed to improve the shortcomings of the standard YSZ material have been described. The presented options concentrate on completely new compositions. Furthermore, new concepts like nanostructured materials and multilayered coatings were discussed. The variety of new, promising solutions in the field of thermal barrier coatings is very encouraging. Especially the double layer systems consisting of YSZ/new TBCs show promising results.

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5. Superconductors and Ferroelectrics



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Superconductivity in the two last decades

S. S. ATA-ALLAH
Reactor & Neutron Physics Department
Nuclear Research Center, Atomic Energy Authority –Cairo Egypt

ABSTRACT

Before 1986, the highest T_c was 23.2K (-249.8 °C/-417.6 °F) in niobium-germanium compounds. Temperatures this low were achieved by use of liquid helium, an expensive, inefficient coolant. Ultralow-temperature operation places a severe constraint on the overall efficiency of a superconducting machine. This, large-scale operation of such machines was not considered practical. But in 1986 discoveries at several universities and research centers began to radically alter this situation. Ceramic metal-oxides compounds containing rare earth elements were found to be superconductive at temperatures high enough to permit using liquid nitrogen as a coolant. Because liquid nitrogen, at 77K (-196 °C/-321 °F), cools 20 times more effectively than liquid helium and in 10 times less expensive, a host of potential applications suddenly began to hold the promise of economic feasibility. In 1987 the composition of one of these superconducting compounds, with T_c of 94K (-179 °C/-290 °F), was revealed to be $YBa_2Cu_3O_7$ (yttrium-barium-copper-oxide). It has since been shown that rare-earth elements, such as yttrium, are not an essential constituent, for in 1998 a thallium-barium-calcium copper oxide was discovered with a T_c of 125K (-148 °C/-234 °F). Between 1986 and 1995 most advances in the field of superconductivity related to the discovery of new superconductor “systems” and compounds. In recent years, except for the discovery of additional elements that will superconduct under extreme high pressure, superconductor news has been mainly about novel way to employ the new ceramic superconductors, innovative fabricating techniques and typical superconductors.

I. INTRODUCTION

Superconductivity, phenomenon displayed by certain conductors that demonstrate no resistance to the flow of an electric current. Superconductors also exhibit strong diamagnetism; that is, they are repelled by magnetic fields. Superconductivity is manifested only below a certain critical temperature T_c and a critical magnetic field H_c , which vary with the material used. The phenomenon was better understood only after strong diamagnetism was detected in a superconductor by Karl W. Meissner and R. Ochsenfeld of Germany in 1933. The basic physics of superconductivity, however, was not realized until 1957, when the American physicists John Bardeen, Leon N. Cooper, and John R. Schrieffer advanced the now celebrated BCS theory, which describes superconductivity as a quantum phenomenon in which the conduction electrons

move in pairs and thus show no electrical resistance. In 1962 the British physicist Brian D. Josephson examined the quantum nature of superconductivity and proposed the existence of oscillations in the electric current flowing through two superconductors separated by a thin insulating layer in a magnetic or electric field. The effect, known as the Josephson Effect, subsequently was confirmed by experiments. Using the quantum effects of superconductivity, devices have been developed that measure electric current, voltage, and magnetic field with unprecedented sensitivity.

The recent discovery of magnesium diboride as a superconductor with transition temperature near 40 K has prompted some discussion of whether this new material might have an impact on the future viability of superconducting digital technology. So, this paper will have two parts;

Part I: gives an overview Josephson junction (JJ) technology.

Part II: deals with one class of HTCS class (123) system to shed more lights on the superconducting mechanism in this important class.

PART I

It is convinced that superconducting Josephson junction (JJ) technology will have a small but important niche in high-performance digital signal and data processing applications for civilian, commercial, and military terrestrial, as well as space deployment. However, before superconductive digital technology can indeed become viable, three conditions must be met:

I- There must be a market-driven demand to employ superconductive digital technology to perform particular functions that cannot be performed by conventional (that is, semiconductor) electronics technology

II- A manufacturable Josephson-junction device and circuit fabrication technology must exist with a suitable broad-based infrastructure

III- Appropriate energy-efficient, reliable, and low-cost cryogenic refrigeration systems suitable to cooling the JJ digital technology in question must be available to produce complete packages that, at the system level, are totally transparent to the cryogenic aspects of this technology. There has been considerable effort over the past thirty years to develop a viable, reproducible, controllable, and manufacturable Josephson-junction technology for use as the active element in digital circuits and systems.

1- Niobium and Niobium Nitride JJ Technology.

For the LTS materials, Nb and NbN, there are practical junction technologies that appear to be manufacturable, stable, and controllable. Much progress has been achieved during the past twenty years to mature and stabilize LTS device and chip level design and fabrication technologies. At the present time, the primary limitation on building chips with greater than 10,000 junctions/cm² appears to be the need for infrastructure, such as clean rooms and lithography equipment, all requiring funds and some manpower resources, which could be done if financial resources were made available. A recent article by Brock, Rowell, and Track (IEEE SPECTRUM, December 2000, p. 40)

3- HTS (that is, cuprates) JJ Technology.

This problem has been addressed fairly extensively, worldwide, during the early part of the 1990s with very modest success and is currently being addressed primarily by the Superconductivity Research Laboratory (SRL) of the International Superconductivity Technology Consortium (ISTEC) in Tokyo and by OXXEL GmbH, in Bremen, Germany. According to results published to date, JJ junctions have been made on YBCO, but they are NOT controllable, predictable, or reproducible, and the variations ("spreads") in device parameters across a chip are too large for any useful level of integration. Some of the reasons that have been offered to explain the difficulty in obtaining reproducible, controllable, and manufacturable HTS JJs with small spreads of parameters on chip include (but are not limited to) issues such as edge-profiling, anisotropy of YBCO, oxygen diffusion at the interfaces between electrodes and the barrier region, very short coherence lengths (of the order of 10 Å, one lattice spacing), and suitable barrier materials with usable values of R_n and J_c . If HTS JJs could be manufactured and if they operated satisfactorily at temperatures near 77 K, they could be cooled by the "least complicated" and smallest input-power systems among the 77 K, 35 K, and 4 K cryocoolers. Recently, there have been speculation and simulations that have suggested that YBCO-like JJ digital circuits might have to be operated in the temperature region near 35 K to minimize thermal upsets of JJ digital devices and thus to realize acceptable bit error rates (BER) for digital processing applications. If indeed HTS JJ digital circuits have to be operated at temperatures near 35 K, the impact on the system would be more complex refrigeration systems and increased electrical input power compared with that required for operation at temperatures near 77 K.

3- Medium Temperature Superconductors (MTS) such as MgB_2 .

The recently discovered materials with T_c near 40 K seem to have properties that are more amenable to junction technology than do the higher temperature cuprate materials. The materials, of which magnesium diboride (MgB_2) was the initially reported one, appear to be s-wave-like, have only slightly anisotropic conduction processes, and have coherence lengths near 50 Å (corresponding to about 10 atomic layers). Since they do not have oxygen as a constituent, diffusion of atoms near the surface or near interfaces between MTS materials and barriers in multilayer structures may not be a problem for these MTS systems. The growth of thin films of MgB_2 with T_c near 39 K and with critical current densities greater than 10^4 A/cm² was reported at the special MgB_2 session on 12 March 2001 at the American Physical Society meeting held in Seattle. Also the fabrication of "good" MgB_2 films was attainable. Nevertheless, since the properties of MgB_2 outlined above resemble many of the desirable properties of the LTS materials (niobium and niobium nitride), one can anticipate that acceptable JJs might be fabricated using this material. If this were to happen, digital circuits operating near 25 K should be practical. (Note that the operations of JJ digital circuits are stable only if they are operated at temperatures less than 2/3 of the transition temperature.) Cryogenic refrigeration systems required for operation at temperatures near 25 K are much less complex and less energy-

A good way to get a feel for comparisons of the refrigeration requirements to cool superconductive digital circuits to temperatures near 4 K, 30 K, or 77 K is to prepare a plot of the coefficient of performance (COP) of cryocoolers [that is, input power at ambient (rejection) temperature divided by the heat removed (in watts) at the cryogenic operating temperature] as a function of operating temperature for various values of percent of Carnot efficiency realized by the given cryocooler (Fig. 1).

SUMMARY

The above information has been presented to review the status of LTS, MTS, and HTS digital technologies and, in addition, cryogenic refrigeration technology. A typical electronic instrument (such as a desktop computer or work station) typically consumes of the order of one to several hundred watts of input power, certainly not kilowatts of input power! The present generation of 1-watt cryocoolers operating near 4 or 10 K usually requires several kilowatts of input power, and this, I maintain, is not and would not be acceptable for most electronic applications.

Therefore the attraction of MTS and HTS digital circuits is the belief that cooling of digital circuits fabricated from these materials to temperatures near 30 K can be done with less than several hundred watts of input electrical power, even with current-day technology, which might be acceptable to the customer. This is why the work on HTS and MTS digital circuit technology is so important.

PART II

In this part the effect of rare-earth ion size effect on resistivity, susceptibility, and superconductivity of $\text{RBa}_2\text{Cu}_3\text{Zn}_x\text{O}_{7-y}$ ($\text{R} = \text{Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd}$)

General Remarks

- 1- Substitution with rare - earth elements on the Y site and with transition or *sp* elements on the Cu site of the high- T_c superconductor (HTSC) $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ is an important method for understanding the mechanism of superconductivity at high temperatures.
- 2- Of special interest for clarifying the effect of impurities on the superconductivity and various characteristics of the HTSC is the substitution for copper by metals such as Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, and Al.(1-43)
- 3- The importance of the two copper sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, Cu (1) in the Cu-O chains and Cu (2) in the CuO_2 planes, for the superconductivity has been reported where;
 - i) Most groups found that nominally trivalent elements [like Ga (1-3,7-19), Fe(1-5,8,10,21-27), Co(1-4,8,10,14-16,18,21-27, and Al(3,4,8,10)] substitute on Cu (1) sites and cause a moderate reduction in T_c ,
 - ii) While nominally divalent dopants [like Zn (6,8,10,18,20-22and28) and Ni(1-4,8,10,11,14 and 19)] primarily occupy the Cu (2) sites and suppress T_c drastically.

With considerable interest in the drastic suppression of T_c , numerous studies on the substitution for Cu in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, with nonmagnetic Zn having definite valence state 2^+ and filled 3d levels have been carried out. Some consistent results were obtained:

- (1) The solution limits is 9-10 %, (4-11,16,17,18,20,29)
- (2) The orthorhombic structure is retained, (1-49)
- (3) The oxygen content is little affected by 10% Zn doping (7-y~6.9) (4,11-15,17), and
- (4) The rate of T_c reduction is 8-15 K/%, the largest known to date. (1,8,19)

For Pr-substituted 123 compounds [on the R sites], $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ($\text{R} = \text{Lu, Yb, Tm, Er, Ho, Y, Dy, Gd, Eu, Sm, and Nd}$, and $0 \leq x \leq 1$), it was established that (44-46);

- 1- The superconducting transition temperature T_c decreases monotonically with increasing Pr concentration x , and,
- 2- At a constant Pr concentration, T_c decreases approximately linearly with increasing radius of the R ions.
- 3- The magnetic ordering temperature T_N of Pr ions was observed to decrease monotonically with increasing R concentration $(1-x)$; and at a constant x , T_N is R ion size dependent.

These results were interpreted qualitatively in terms of the hybridization between the local states of the Pr ion and the valence-band states of the CuO_2 planes.

Also, in the Ga-doped [on Cu (1) sites] for $\text{RBa}_2\text{Cu}_{3-x}\text{Ga}_x\text{O}_{7-y}$ systems (where $R=\text{Yb, Er, Y, Dy, Gd, Eu, and Nd}$, at $x=0.0, 0.05, 0.1, 0.15, 0.2$, and 0.3), it is also found the normal state resistivity ρ_n , and the superconducting T_c are dependent upon the rare- earth ion size. It was suggested that a decrease in the density of states $N(E_F)$ or localization of carriers due to Ga substitution are the possible mechanisms for suppression of superconductivity (47,48).

Since most groups observed that Zn substitutes [on the Cu (2) sites] in 123 systems it was very interesting to study the effect of Zn doping on the properties of different rare-earth 123 compounds. In this work a detailed investigation of the structural properties, resistivity ρ , dc susceptibility χ' and superconductivity of the Zn-substituted $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ systems ($R=\text{Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd}$) with $0 \leq x \leq 0.3$.

EXPERIMENT

$\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ ($R=\text{Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd}$) with $0 \leq x \leq 0.3$ samples were prepared by solid-state reaction method, were:

- 1- Powders of R_2O_3 , BaCO_3 , CuO , and ZnO with a purity $\sim 99.99\%$ were mixed in agate mortar, and calcined at 915°C for 24 h.
- 2- The resultant powders were reground and refired to improve the homogeneity.
- 3- After a final careful grinding these powders were pressed with 4 kbar into $5 \times 30 \times 1\text{-mm}^3$ rectangular bars.
- 4- These bars were sintered in oxygen flow at $925\text{-}930^\circ\text{C}$ (except $R=\text{Yb}$ at 920°C) for 72 h followed by additional annealing at 680°C for 10 h and 400°C for 10 h.
- 5- Finally these bars were furnace cooled in oxygen flow to room temperature over about 10 h.

X-ray Powder diffraction (XRPD) studies at room temperature using $\text{CoK}\alpha$ radiation ($\lambda = 1.788970 \text{ \AA}$) were carried out for all samples.

The normal-state resistivity and superconducting transition temperature T_c were measured by standard four-probe technique Magnetization was measured using a quantum design magnetometer at both zero-field cooling (ZFC) and field cooling (FC) in a magnetic field of 50e.

RESULTS AND DISCUSSION

XRPD patterns indicate that:

- 1- The compounds with $0 \leq x \leq 0.3$ and $R = \text{Er, Y, Dy, Gd, Eu, Sm and Nd}$ have a single-phase orthorhombic perovskite like $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ structure.
- 2- While the samples with $R = \text{Yb}$ and at $x \sim 0.1$ have weak extra peaks corresponding to a few percent of foreign phase.
- 3- Detailed x-ray powder diffraction measurements show that the structure remains orthorhombic throughout the substitution range ($0 \leq x \leq 0.3$). [Table 1]

TABLE I. The lattice parameters a , b , and c of $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ ($R = \text{Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd}$) at various Zn concentration x . The last numbers of each a , b , and c were estimated.

Rare earth	Lattice parameters ($\text{\AA}$)	Zn Content x							
		0	0.01	0.02	0.04	0.06	0.08	0.1	0.15
Yb	a	3.8766	3.8687	3.8749	3.8807	3.8821	3.8787		
	b	3.8014	3.8009	3.8032	3.8084	3.8054	3.8094		
	c	11.6460	11.6558	11.6509	11.6557	11.6536	11.6598		
Er	a	3.8776	3.8787	3.8758	3.8757	3.8799	3.8763	3.8767	3.8793
	b	3.8094	3.8085	3.8055	3.8084	3.8093	3.8070	3.8075	3.8084
	c	11.6549	11.6592	11.6466	11.6525	11.6495	11.6501	11.6498	11.6586
Y	a	3.8860	3.8860	3.8877	3.8858	3.8860	3.8861	3.8859	3.8873
	b	3.8176	3.8178	3.8198	3.8172	3.8169	3.8172	3.8179	3.8182
	c	11.6688	11.6645	11.6651	11.6635	11.6635	11.6658	11.6673	11.6664
Dy	a	3.8945	3.8891	3.8953	3.8868	3.8865	3.8848	3.8869	3.8867
	b	3.8362	3.8258	3.8290	3.8212	3.8227	3.8215	3.8218	3.8290
	c	11.6840	11.6731	11.6724	11.6742	11.6773	11.6798	11.6756	11.6994
Gd	a	3.8979	3.9056	3.9076	3.9091	3.9076	3.9073	3.9095	3.9092
	b	3.8384	3.8422	3.8472	3.8438	3.8452	3.8467	3.8443	3.8469
	c	11.7026	11.7028	11.7156	11.7168	11.7218	11.7219	11.7218	11.7275
Eu	a	3.8975	3.8922	3.8983	3.8990	3.8996	3.9017	3.8962	3.8999
	b	3.8395	3.8345	3.8394	3.8394	3.8401	3.8427	3.8386	3.8400
	c	11.7090	11.7137	11.7179	11.7159	11.7165	11.7168	11.7174	11.7186
Sm	a	3.9028	3.9046	3.9060	3.9059	3.9066	3.9034	3.9089	3.9134
	b	3.8487	3.8494	3.848	3.8507	3.8498	3.8482	3.8534	3.8558
	c	11.7325	11.7367	11.7361	11.7334	11.7356	11.7373	11.7372	11.7354
Nd	a	3.9183	3.9125	3.9146	3.9166	3.9105	3.9147	3.9158	3.9174
	b	3.8608	3.8633	3.8604	3.8624	3.8602	3.8566	3.8586	3.8589
	c	11.7725	11.7741	11.7735	11.7786	11.7704	11.7884	11.7796	11.7725

- 4- The lattice parameters a , b , and c are very close to those of undoped $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$ ($R = \text{Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd}$).
- 5- The orthorhombicity $(a-b)/(a+b)$ seems to be independent of the Zn concentration x in the range $0 \sim x \sim 0.3$. This indicates that the oxygen vacancy order or the linear chain structures of the Cu(I)-O sites remains intact. Therefore it may be inferred that Zn

replaces Cu in the planes adjacent to the R planes rather than in the Cu-O chains, thus retaining the orthorhombic structure.

From temperature dependence of resistivity of $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ systems with Zn concentrations $x=0.01$ and 0.1 it is clear that: (Fig. 2)

- 1- The decrease of T_c with increasing Zn substitution levels is clearly demonstrated.
- 2- The samples of $R = \text{Yb, Er, Y, and Dy}$ are metallic in the substitution range $0 \sim x \sim 0.1$, with a positive temperature coefficient of resistivity (TCR).
- 3- For systems where $R = \text{Gd, Eu, Sm and Nd}$ in the vicinity of $x = 0.06$ for Gd and Eu, and 0.02 for Sm and Nd, the variation of ρ with lowering temperature tends to become flat
- 4- At higher substitution levels the normal-state resistivity presents a semiconducting character with a negative temperature coefficient of resistivity (TCR), and causes a significant degradation in superconductivity.

From the temperature dependence of ρ for $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ with $x=0.3$, (Fig. 3) an obvious trend is observed where the normal-state resistivity ρ increases with increasing ion size of R .

To compare the normal-state resistivity at the same Zn substitution level in different $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ systems, (Table 2) lists the radius of R ions, and the data of ρ at 290, 200, and 100 K, with $x= 0.02$, and 0.08 , where:

TABLE II. The dependence of the normal-state resistivity ρ of $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ at 290, 200, and 100 K, with Zn content $x=0.02$ and 0.08 , where all the TCR's are positive (metallic behavior), on the ionic radius of the element R ($R=\text{Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd}$). The superconducting transition temperature T_c is also present.

Zn content x	Rare earth	Ionic radius (pm)	$T_{c, \text{mid}}$ (K)	Resistivity at 290 K	ρ (m Ω cm) 200 K	100 K
0.02	Yb	85.8	83.67	0.85	0.581	0.351
	Er	88.1	84.94	0.807	0.588	0.367
	Y	89.3	85.1	0.781	0.565	0.35
	Dy	90.8	85.07	0.887	0.661	0.435
	Gd	93.8	86.5	0.956	0.742	0.528
	Eu	95.0	86.64	1.355	1.088	0.797
	Sm	96.4	86.5	1.709	1.404	1.089
	Nd	99.5	86.14	4.464	3.911	3.899
0.08	Yb	85.8	70.92	1.284	0.927	0.608
	Er	88.1	62.19	0.983	0.745	0.522
	Y	89.3	61.82	1.06	0.814	0.589
	Dy	90.8	60.34	1.108	0.868	0.665
	Gd	93.8	55.11	1.224	0.957	0.791
	Eu	95.0	53.7	1.602	1.362	1.212
	Sm	96.4	51.8	1.860	1.629	1.597
	Nd	99.5	36			

- 1- All TCR's are positive (metallic behavior).
- 2- At constant x ρ increases with increasing ionic radius of R , which means that the R plane affects the carrier localisation or the effect of Zn scattering.

- 3- For $x=0.3$ and $R=Dy$, Gd, Eu, Sm, and Nd, and for $x = 0.2$, $R = Sm$ and Nd, the samples were not superconducting down to 4.2K, and showed only a semiconductor like character.
- 4- At low temperatures the results can be interpreted in terms of Mott variable range hopping law (VRH), and follow a universal behavior, $\rho(T)=\rho_0 \exp(T/T_0)^{-1/4}$ (49).

Near room temperature ρ can be fitted by an exponential function of $1/T$, $\rho(T) = \rho_3 \exp(E_3/kT)$, indicating that at high temperatures (~ 290 K) contribution to conductivity comes from nearest-neighbor hopping (NNH) (50).

The superconducting transition width ΔT_c , which is taken as the difference between $T_{c \text{ mid}}$ and $T_{c \text{ zero}}$ (the temperature at which the resistivity drops to zero), where:

- 1- Increases with increasing Zn concentration for each R , and also with increasing ionic radius of the rare-earth element when the Zn concentration is kept constant.
- 2- The values of the critical concentration X_{cr} required to suppress T_c to zero are estimated to be around 0.21, 0.19, 0.17, and 0.11 for $R=Gd$, Eu, Sm, and Nd, respectively.
- 3- The rate of change of resistivity with x remarkably increases at the critical concentration X_{cr} indicating that semiconductor like behavior accompanies the destruction of the superconducting phase.
- 4- These results indicate that variations of the Zn concentration influence the electronic states of the materials: the density of states, or the mobility of the charge carriers.

The dc susceptibility per mol χ as a function of temperature for $DyBa_2Cu_{3-x}Zn_xO_{7-y}$ samples (as an example for all systems discussed above) with $x=0, 0.02, 0.04, 0.06, 0.08$, and 0.1 , at both zero-field cooling (ZFC) and field cooling (FC) (Figs. 5 and 6) shows:

- 1- The transition temperatures $T_{c \text{ mag}}$ evaluated are well consistent with $T_{c \text{ mid}}$ deduced from resistivity measurements.
- 2- Doping with Zn not only suppresses T_c , but also reduces the fractions of diamagnetic shielding, indicating the reduction in the fraction of superconducting materials or phase separation in samples with higher Zn content in spite of the fact that XRD measurements showed single-phase structures in these samples.
- 3- The dc susceptibility per mol χ versus temperature of $RBa_2Cu_{2.9}Zn_{0.1}O_{7-y}$ at ZFC for $R=Yb, Er, Dy, Eu, Sm$, and Nd, demonstrates that at a constant Zn concentration $x=0.1$ either $T_{c \text{ mag}}$ or the fraction of magnetic shielding of the $RBa_2Cu_{2.9}Zn_{0.1}O_{7-y}$ samples is changed by varying the rare-earth element R .
- 4- The samples with larger R ion radius have lower T_c and a small fraction of superconducting phase.

A plot of $T_{c \text{ mid}}$ and $T_{c \text{ mag}}$ versus ionic radius of the rare- earth elements R in $RBa_2Cu_{3-x}Zn_xO_{7-y}$ ($R=Yb, Er, Y, Dy, Gd, Eu, Sm$, and Nd) (Fig. 7) shows.

- 1- A closely linear relationship between T_c and the radius of R ions at low concentrations of Zn can be observed.
- 2- With rising Zn substitution ($x > 0.06$), the suppression of T_c is apparently enhanced by increasing the ionic radius of the rare-earth elements R .

The effect of ion size on T_c for Zn-doped systems shown are similar to the observations in Pr-doped $R_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ($R = \text{Lu, Yb, Tm, Er, Ho, Y, Dy, Gd, Eu, Sm, and Nd}$) (44-46) and in Ga-substituted $R\text{Ba}_2\text{Cu}_{3-x}\text{Ga}_x\text{O}_{7-y}$ ($R = \text{Yb, Er, Y, Dy, Ga, Eu, and Nd}$) systems (47,48). However, Pr substitutes on R sites and the concentration of R is changed by introducing Pr, whereas Ga and Zn is replaced on the Cu(1) and Cu(2) sites, respectively, and the copper content is reduced by Ga- and Zn doping. For a specific *RBCO* system with different Pr-, Ga, or Zn doping, the rates of T_c suppression dT_c/dx and the critical impurity concentration X_{cr} are different, implying different mechanisms for the degradation of superconductivity by various impurities.

Suppression of superconductivity by Zn doping has been intensively discussed. Several suspected mechanisms for T_c suppression can be ruled out here:

- (1) There is no correlation between T_c and orthorhombic to tetragonal (O-T) transition, since orthorhombic structure is retained in 10% Zn-replaced *RBCO* systems.
- (2) Because the oxygen stoichiometry remains nearly unchanged in 10% Zn-doped (11-13) and 16% Zn-doped GdBCO systems (42), the reduction of T_c is not caused by oxygen deficiency.
- (3) Due to the nonmagnetic nature of Zn ions the reduction of T_c by the magnetic moment of the dopant observed in Pr-doped systems is unlikely. It is estimated that a moment-carrier exchange $J_{eff} = 20$ meV, which is more than an order of magnitude too small to account for the suppression of T_c in Zn-doped YBCO via Abrikosov-Gorkov pair breaking. They suggested an alternative explanation of pair breaking by strong potential scattering from the Zn impurity sites that require d-wave pairing (29)

The results of T_c depression due to Zn substitution can possibly be ascribed to:

- 1- The effect of disorder or a reduction in the carrier concentration. The magnetic penetration depth $\lambda(T)$ measurements carried out on Zn-doped YBCO films (51) and on magnetically aligned powders show that Zn doping has a particularly strong increase in $\lambda(0)$, implying that disorder results in decreasing superconducting density of states.
- 2- The substitution of Zn^{2+} (having a closed shell $3d^{10}$) for Cu possibly reduces the Cu 3d-hole or slightly changes the state of hybridization between Cu 3d and O 2p, thus decreasing the density of states at Fermi energy $N(E_F)$. Since Zn ions are in the same valence state as Cu^{2+} , Zn will not alter the charge balance within the CuO_2 plane, but would severely disorder and disturb the alignment of $\text{Cu}(3d_{x^2-y^2})$ and $\text{O}(2p_d)$ orbitals,

which would result in carrier localization in the CuO_2 planes. The localization effect arising from Zn substitution can then account for the metal-semiconductor *transition* and thus the destruction of superconductivity.

The ion size effect was established for Pr-doped (**on Y sites**) systems, and also found for Ga-doped [**on the Cu(I) sites in Cu-O chains**] systems.

In the present work we find that this R ionic size effect also exists in Zn-doped [on the Cu(2) sites in Cu-O_2 planes] $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ systems. Although the mechanism of the rare-earth ion size effect on T_c and ρ by Zn doping is not well understood yet, we propose a possible interpretation in terms of Mott's spin- bipolaron model (31-48).

Mott (31,52) supposes that in the copper oxide *p-type* superconductors the carriers (O $2p$ holes) form bipolarons (bosons) above and below T_c . The spin on an oxygen hole is locked antiparallel to one of the Cu $3d^9$ spins. Two of these polarons form a bipolaron (boson) of zero moment with a binding energy of -0.3 eV. The motion of bipolarons is diffusive, activated by spin flip. In the superconducting state the holes form a degenerate gas of bosons, interacting but not strongly overlapping as do the BCS pairs. At $T \geq T_c$ the Bose gas becomes nondegenerate (above T_c the current is carried by a nondegenerate gas of bosons). The bosons are in an impurity band, so that boson states up to a limiting energy E_c are Anderson localized. On account of the strong repulsion between the bosons, Mott proposes that not more than one boson can be in a given state, even above the mobility edge. The energy up to which states are singly occupied, behaving like a Fermi energy, is named E_B (or pseudo- Fermi-energy E_F). If E_B lies in the range of localized states, the material cannot be a superconductor, and the bosons cannot move. Only if E_B lies above E_c will a superconductor form. If states are still localized, the conduction should be due to variable range hopping. This model was used to interpret experimental observations on copper oxide superconductors: the constant value of specific heat over temperature, C_v/T , the small entropy at superconducting transition (much smaller than $Nk \ln 2$), the linear dependence of resistivity on temperature (above T_c , $\rho \propto T$), the Hall effect, the thermopower, the observed Fermi surface, and so on.

For Zn-doped YBCO, Mott supposes that the effect of zinc, which produces disorder in the planes, is to prevent pairing and to render the polarons immobile (Anderson localization). The presence of zinc will result in an increase in the mobility edge E_c , moving it up eventually to E_B , destroying the superconductivity.

In this case for an insulating compound $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$, where x is large enough to suppress T_c to zero, the pseudo-Fermi-energy E_B is lower than E_c . A transition of the Anderson type of metallic behavior should occur when E_B crosses the mobility edge as the content of zinc is reduced. As $x < x_{CI}$ the bosons above the mobility edge produce the superconductivity. The rare-earth ion size effect on T_c of $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ observed in this work could then be ascribed to

the ion size effect on E_c and/or E_B at constant x . This means that for the same amount of zinc replacing copper, the range of localized states is affected by the R plane. An increase in the ionic size of R will move the mobility edge E_c upwards and/or will lower E_B in $RBa_2Cu_{3-x}Zn_xO_{7-y}$ systems.

Conclusion

Systematically studies for the effect of Zn doping on the resistivity ρ , dc susceptibility χ , and superconducting T_c of $RBa_2Cu_{3-x}Zn_xO_{7-y}$ systems ($R=Yb, Er, Y, Dy, Gd, Eu, Sm$, and Nd , and $0 \leq x \leq 0.3$), found that:

- 1- Zn atoms substitute more likely on the Cu(2) sites,
- 2- Zn doping in these systems causes a rapid nearly linear decrease in T_c as Zn content increases, and
- 3- The reduction of T_c for $RBa_2Cu_{3-x}Zn_xO_{7-y}$ depends on the ionic radius of the rare-earth element R . The suppression of superconductivity by zinc and the rare-earth. Ion size effect on T_c in these systems is interpreted in terms of a Mott spin bipolaron model.

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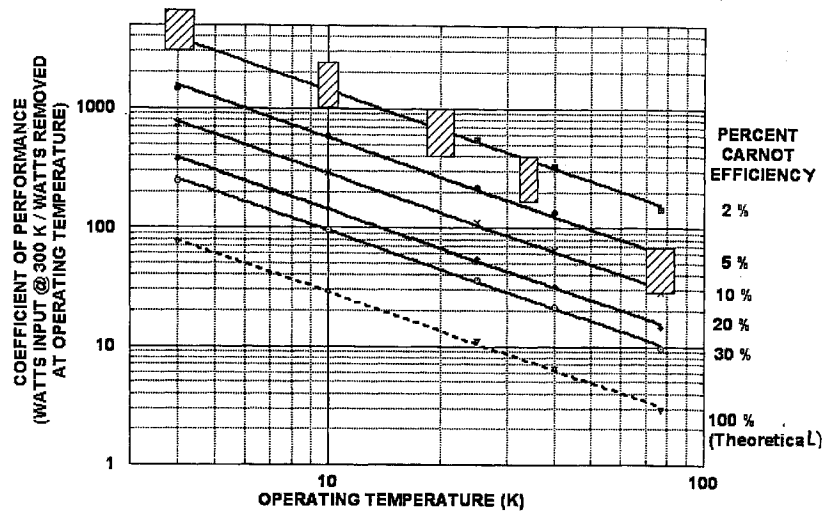


Fig 1 Coefficient of performance of 1-watt cryocooler as a function of operating temperature for various values of Carnot efficiency. The shaded areas indicate the range of input powers for real cryocoolers operating at the indicated operating temperature.

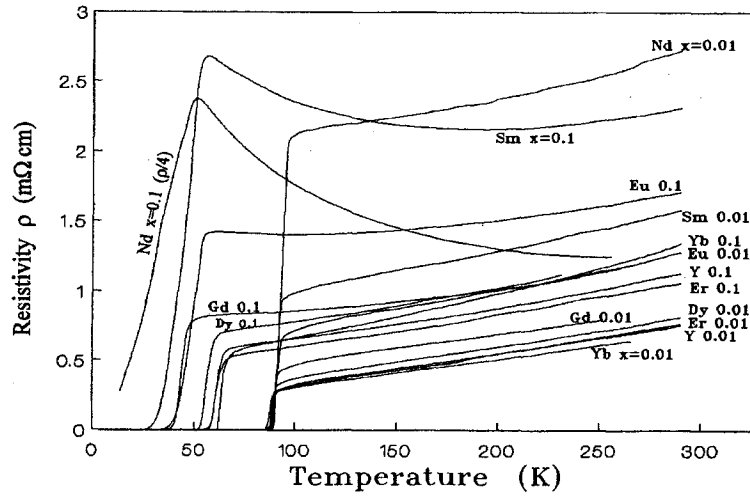


Fig. 2 Temperature dependence of resistivity ρ of $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ ($\text{R}=\text{Yb}, \text{Er}, \text{Y}, \text{Dy}, \text{Gd}, \text{Eu}, \text{Sm}, \text{and Nd}$) systems with Zn concentrations $x=0.01$ and 0.1 .

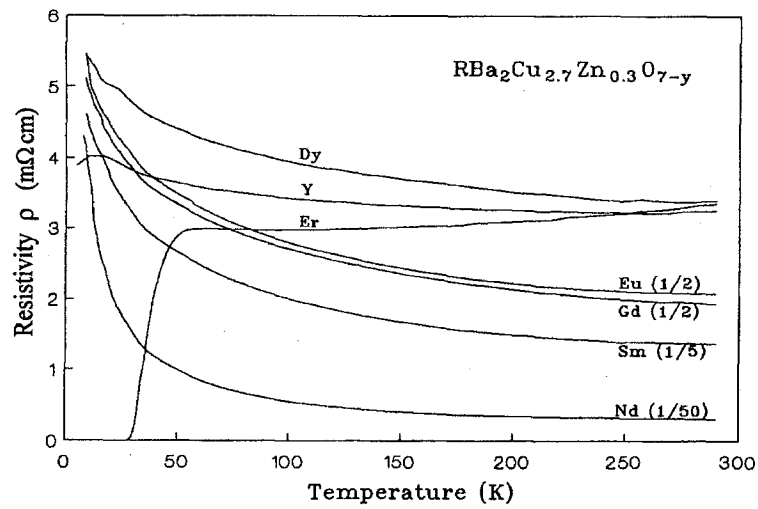


Fig 3 Resistivity ρ vs temperature of $\text{RBa}_2\text{Cu}_{2.97}\text{Zn}_{0.3}\text{O}_{7-y}$ ($\text{R}=\text{Yb}, \text{Er}, \text{Y}, \text{Dy}, \text{Gd}, \text{Eu}, \text{Sm}, \text{and Nd}$).

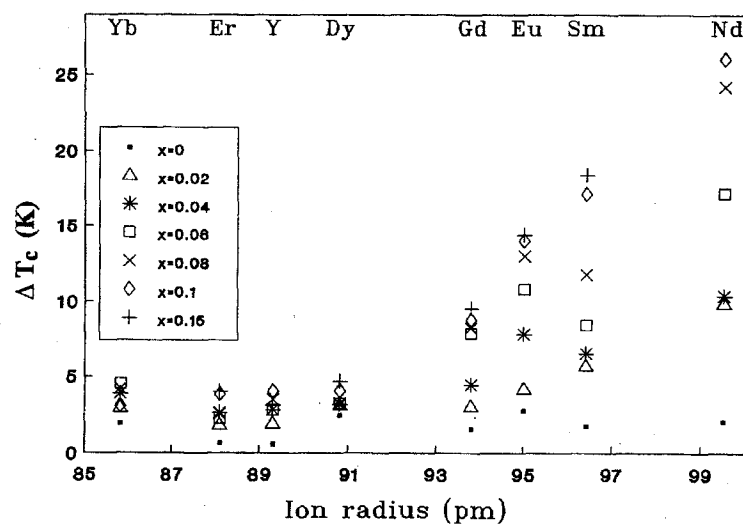


Fig 4 The transition width ΔT_c , vs the ionic radius of rare-earth element R at various Zn content x for $\text{R}\text{Ba}_2\text{Cu}_{2.97}\text{Zn}_{0.3}\text{O}_{7-y}$ (R=Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd).

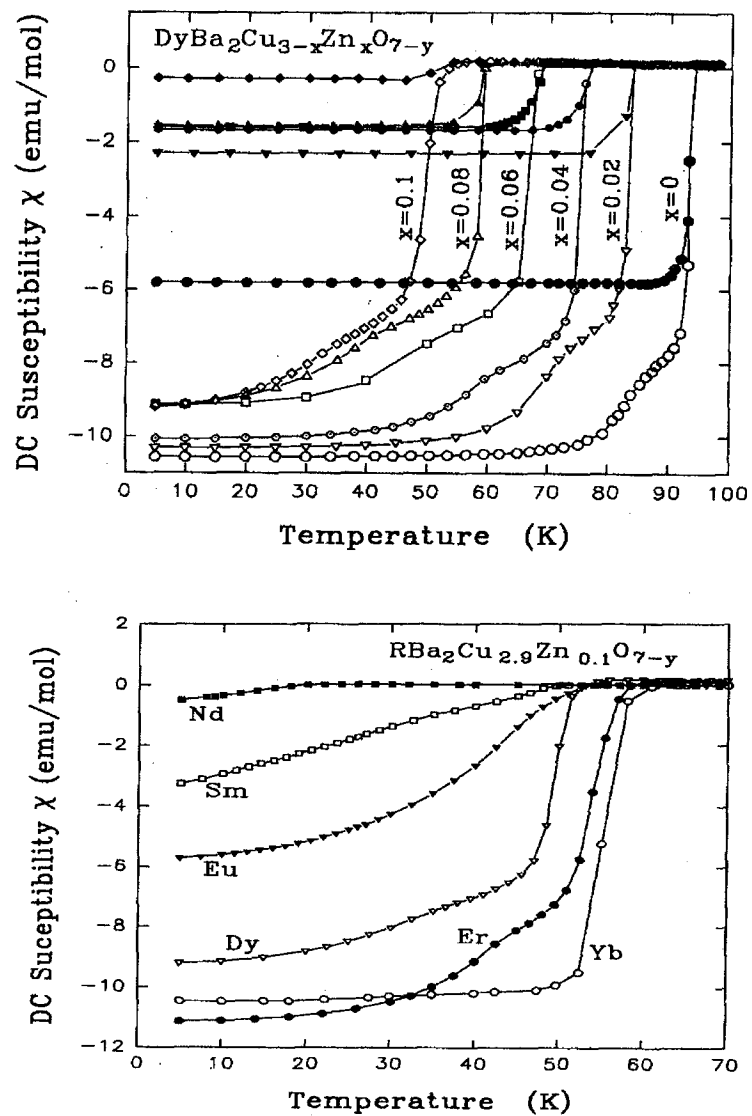


Fig 5 dc susceptibility per mol χ of $\text{DyBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ ($x=0, 0.02, 0.04, 0.06, 0.08$, and 0.1) the upper part, and $\text{RBa}_2\text{Cu}_{2.9}\text{Zn}_{0.1}\text{O}_{7-y}$ ($R=\text{Yb}, \text{Er}, \text{Dy}, \text{Eu}, \text{Sm}$, and Nd) the lower part.

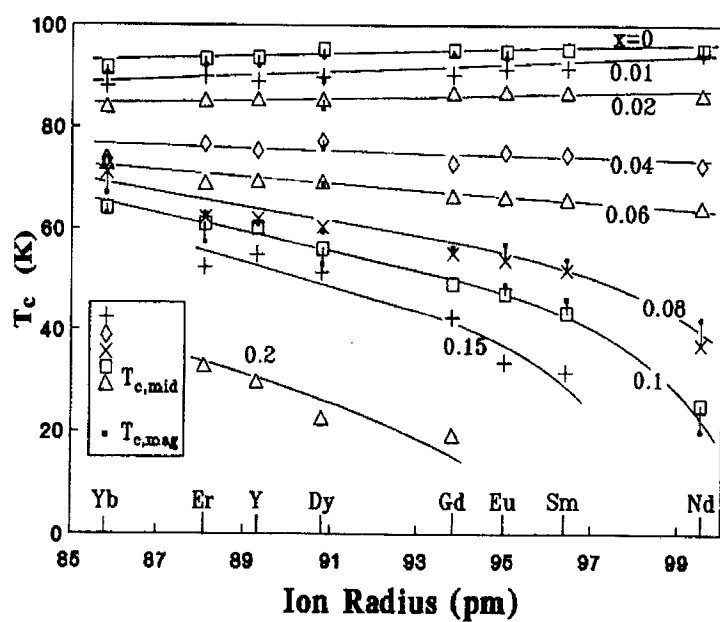


Fig6 plot of $T_{c,\text{mid}}$ and $T_{c,\text{mag}}$ versus ionic radius of the rare- earth elements R in $\text{RBa}_2\text{Cu}_{3-x}\text{Zn}_x\text{O}_{7-y}$ ($R=\text{Yb}$, Er, Y, Dy, Gd, Eu, Sm, and Nd) at different Zn concentrations.

Possible observation of a glassy ferroelectric: $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{2.8}\text{K}_{0.2}\text{O}_z$

A. A. Bahgat and T. M. Kamel

Department of Physics, Faculty of Science, Al-Azhar University, Nasr City 11884, Cairo, Egypt

(Received 23 May 2000; revised manuscript received 16 August 2000; published 11 December 2000)

A glass sample of composition $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{2.8}\text{K}_{0.2}\text{O}_z$ was prepared by the conventional quenched-melt technique. The as-quenched sample has been confirmed to be amorphous by x-ray diffraction measurements. The scanning electron microscopy shows no sign of crystalline grain precipitation. Differential thermal analysis indicates a prominent endotherm at 530 K in addition to the glass transition at 607 K and crystallization at 717 K and melting at 1043 K. This extra endothermic peak could possibly be identified as due to a ferroelectric to paraelectric phase transition. This possibility was explored by performing electrical measurements, which include dielectric constant trace, polarization, and hysteresis loops measurements as a function of temperature. It was also found that the transition is irreversible if the glass-transition temperature was reached.

DOI: 10.1103/PhysRevB.63.012101

PACS number(s): 77.84.Bw

In recent papers, Zhang and Widom^{1,2} proposed a mean-field theory that predicts ferroelectric phases in dipolar systems that lacked any specific spatial correlations, provided that the density of the particles was above a critical value. They considered an amorphous solid of dipolar hard spheres where the particles were free to rotate, but were frozen at random sites. Their prediction of ferroelectric phases in dipolar systems that lack any specific spatial correlations suggests that well-tuned short-range structure may not be necessary for ferroelectric phase formation. However, applying molecular dynamics and Monte Carlo computer simulations predicted that it is possible to have ferroelectric states without fine-tuned positional correlations.³ It was predicted also that if a ferroelectric phase is to exist in a positionally random system, the long-range spatially independent correlations arising through the reaction field must dominate the short-range position sensitive correlations, which generally act to frustrate ferroelectric order.

In an older study, ferroelectric glass concept was studied with no objections found.⁴ A simple microscopic model was set up, describing the possible occurrence of a ferroelectric instability in an insulating glassy matrix. In studying dielectric soft glasses such as $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, LiTaO_3 , and LiNbO_3 different behavior on approaching the crystallization temperature T_x is observed.^{5,6} The first $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ appears to be paraelectric throughout and the dielectric constant rises monotonically with increasing temperature to exhibit a sharp cusp at T_x . While LiTaO_3 has a similar response as a function of T except that the magnitude of the dielectric constant is much larger and anomaly at T_x is observed and may peak below the crystallization instability. If so, this could indicate the existence of a polar glassy phase. The LiNbO_3 glass, on the other hand, exhibits a double peaked anomaly with extremely high values ($>10^5$) for the dielectric constant. This indicates not only a polar glassy phase but also a polar glassy phase transition.⁶ The possibility that the lower-temperature peak does indeed mark a ferroelectric Curie temperature T_c remains an intriguing possibility. However, the role of short-ranged spatial correlations on ferroelectric phase formation is still not well understood. Accordingly, the possibility of

ferroelectric ordering in glassy state that has not been realized experimentally might not be impossible.

Although theoretical and experimental studies have been extended concerning the possibility of glassy ferroelectric, to our knowledge a bulky melt quenched glassy ferroelectric material was not made. Ferroelectricity reports on thin films, ball milled nanocrystalline powder, heat-treated glass ceramic, and sol gel can be found.⁶⁻¹⁰

In a number of recent systematic studies,¹¹⁻¹⁴ glass systems of the main former Bi_2O_3 were considered and applied to prepare melt quenched glasses as precursor to superconducting glass-ceramics. Glasses of compositions $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_{16}$ and $\text{Bi}_2\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, doped with Na shows many interesting dielectric properties, although without any anomalies.^{13,14}

In the present work x-ray diffraction, scanning electron microscopy (SEM) and differential thermal analysis (DTA) were applied to identify the glassy nature of the sample. Dielectric constant ϵ , polarization P , and hysteresis loops (E - P) measurements were used to identify the electrical properties of the sample as a function of frequency and temperature.

A glass sample of the composition $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{2.8}\text{K}_{0.2}\text{O}_z$ was prepared by the quenched melt technique from reagent grade Bi_2O_3 , Pb_2O_3 , SrCO_3 , CaCO_3 , CuO , and K_2CO_3 . The batch was melted at 950 °C for 30 min during which the melt was stirred to improve the homogeneity. The melt was then poured and rapidly quenched between two copper plates; hammer and anvil. Sheets of opaque black glass samples (0.5 mm thick) were obtained. Grounded powder of the as-quenched glass sample was examined by x-ray powder diffraction using Mo-K_α radiation. Optical microscope of the polished surface of the sample, as well as scanning electron microscopy, using a JOEL-JSM-5400 scanning microscope were used to examine the surface of the glass sample for possible crystallization.

On the other hand, real ϵ' and imaginary ϵ'' components of the dielectric constant $\epsilon^* = \epsilon' + j\epsilon''$ measurements were performed at the frequency range 0.12–100 kHz, and in the temperature range 300–700 K. Silver painted electrodes were pasted on the two faces of a polished sample. The di-

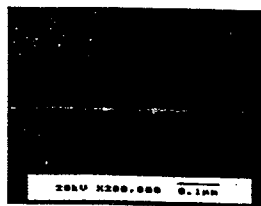
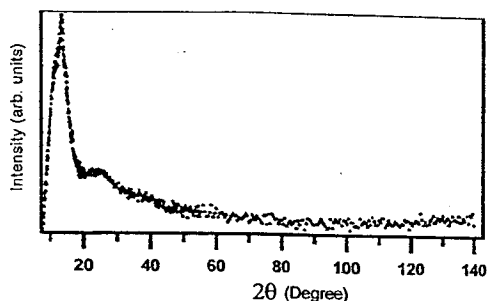


Plate 1

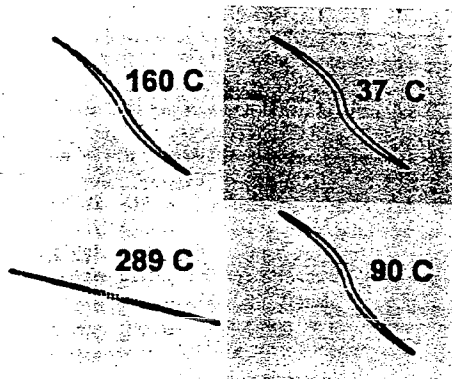


Plate 2

FIG. 1. X-ray diffraction pattern of the as quenched glass sample, using Mo- K_α radiation. Plate 1: SEM micrograph of the quenched glass sample. Plate 2: Representative hysteresis loops of the as-quenched glass sample at different temperatures indicated in $^{\circ}\text{C}$, up to $T > T_c$. Applied frequency is 70 Hz and applied electric field is 1.5 kV/cm.

electric constant was obtained using a (RLC) bridge; Stanford Res. Model SR-720. The sample temperature was measured by a (chromal-alumal) type K thermocouple which is placed as close as possible to the sample. Ferroelectric hysteresis loops were observed using a Sawyer-Tower circuit¹⁵ at temperatures up to 700 K and at a frequency of 70 Hz. The same circuit was used as well for the measurement of the temperature dependence of the polarization over the temperature range 300–700 K. The polarization as a function of electric field (E - P) characteristic was measured at room

TABLE I. Important transition temperatures as obtained from the DTA thermogram for the as quenched glass sample. T_c is the Curie point, T_g is the glass transition, T_x is the crystallization, and T_m is the melting temperature, respectively.

T_c (K)	T_g (K)	T_x (K)	T_m (K)
530	607	717	1043

temperature under ac electric field of frequency 70 Hz with amplitude reaching 1.6 kV/cm.

Figure 1 shows the x-ray diffraction of the as-quenched glass sample. It can be seen that there are only the broad diffraction peaks characteristic of glassy structure. Similar patterns were obtained for glasses of comparable constituents.^{11,12,14} On the other hand, a SEM micrograph is shown in plate 1. It is seen that there is no crystalline precipitation. A similar result was observed on comparable glass.¹⁶

The glassy state of the as-quenched sample was monitored also by DTA. The sample was heated from room temperature up to 900 $^{\circ}\text{C}$ with a rate of 20 $^{\circ}\text{C}/\text{min}$. The DTA thermogram shows three different endothermic and one exothermic transitions. These were identified as a glass transition temperature (T_g), melting temperature (T_m), and an extra peak which is usually not observed with conventional glasses. This endothermic peak is at a temperature lower than T_g and is designated from the results of the present work as due to a ferroelectric to paraelectric phase transition (i.e., Curie's point T_c). A fourth peak that is exothermic indicates the crystallization temperature T_x of the glass. Table I summarizes the results of the DTA measurement shown in Fig. 2(a). The DTA thermogram indicates that the endothermic peak at $T_c = 530 \pm 2$ K, is due to a first-order phase transition while the sample is still in its glassy state, where $T_c \ll T_g < T_x$, as shown. Similar observation is familiar in the field of ferromagnetic metallic glasses.¹⁷

Usually a ferroelectric to paraelectric endothermic peak is observed in DTA thermograms only after devitrifying the amorphous samples.^{9,10} It was also evident that the ferroelectric behavior depends on the size of the precipitating crystallites following heat treatment, where the transition at the Curie temperature T_c becomes increasingly diffuse and may vanish with decreasing the grain size within the nanometer scale.^{9,18,19} A comparable behavior is familiar in the field of superparamagnetic materials.

Figure 2(b) shows the variation of the dielectric constant as a function of temperature at different applied frequencies. It can be seen that there are mainly two different maximums with dielectric constant ranging from 6.3×10^4 to 1.6×10^5 . The maximum at 525 ± 5 K is evidently an indication that the sample is not only in a polar phase but actually it is in a polar glassy phase transition. While the maximum at 606 K coincides with the inflection point of the DTA thermogram, Fig. 2(a) indicating the glass transition temperature. This observation may be explained on the basis of the microscopic model proposed by Glass *et al.*⁶

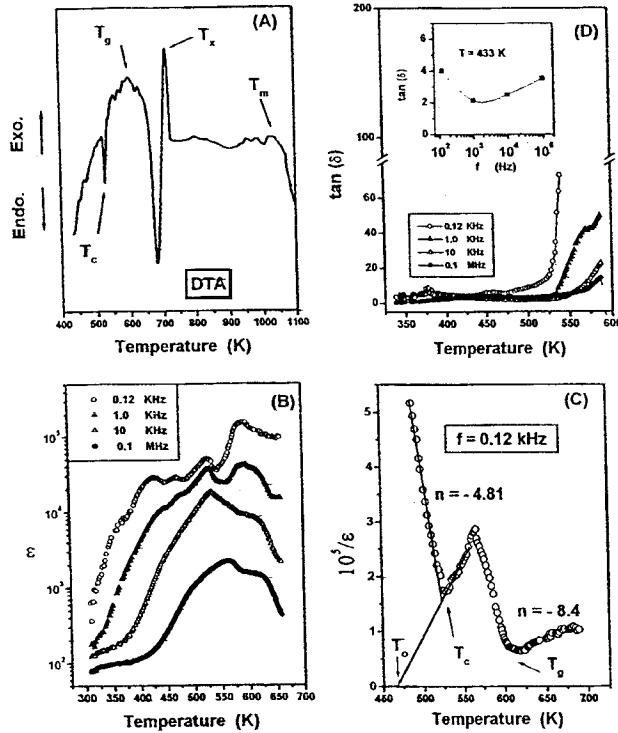


FIG. 2. Experimental results of the as-quenched glass sample $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{2.8}\text{K}_{0.2}\text{O}_2$. (a) The DTA thermogram, showing different transitions. (b) Dielectric constant as a function of temperature at applied frequency of 0.12–100 kHz. (c) Inverse dielectric constant as a function of temperature showing the values of n and T_0 of the Curie's Eq. (1) at frequency 0.12 kHz. (d) Loss tangent as a function of temperature, the inset shows a representative example of the variation of $\tan(\delta)$ as a function of frequency.

The fact that DTA data shows an endothermic peak at this same temperature could support the conclusion that our glass sample is actually ferroelectrically ordered below 525 K, namely, the Curie point T_c . It is also evident from Fig. 2(b) that the temperature position of this dielectric peak maximum is almost frequency independent, indicating that there are insignificant relaxational effects.

On the other hand, the dielectric constant data could be treated according to the Curie-Weiss relation

$$\epsilon = \frac{C}{T - T_0}. \quad (1)$$

Here $C = 3.87 \times 10^6$ K is the Curie constant and $T_0 = 470$ K is the extrapolated intersection of the high-temperature part of the plot with the temperature axis as shown in Fig. 2(c). However, to identify the order of this transition it is usually a general practice to find out the ratio n of the slopes $\partial(1/\epsilon)/\partial T$ below and above T_c , which is ($n = -4.81$), see Fig. 2(c). This value indicates according to the theory of Devonshire²⁰ that the observed transition is of first-order type in agreement with the above DTA results and is due to metastability at the transition. While if the same criteria is applied to the second peak at about 607 K which was iden-

tified as due to the glass transition T_g ($n = -8.4$) indicating a clear first-order transition. It is observed that the Curie constant is one order of magnitude higher than the corresponding values of crystalline materials, e.g., $C = 1.8 \times 10^5$ K for BaTiO_3 ,²⁰ this may be due to the glassy nature of our sample.

Figure 2(d) shows the variation of the loss in terms of $\tan(\delta) = \epsilon''/\epsilon'$. It is seen that the loss is of the same order of magnitude as observed usually in Bi-Cu glasses of comparable compositions^{12,14,21}. While it increases considerably as the glass transition temperature, T_g , is approached. On the other hand as can be seen from the insert of Fig. 2(d) the loss is almost frequency independent at 434 K, indicating insignificant relaxational effects.

Plate (2) shows representing examples of the hysteresis loops as a function of temperature. It is seen that the loop collapse as the temperature is increased up to the Curie point. These loops prove the ferroelectricity nature of the present a quenched amorphous sample. It was also found that the transition is reversible if the glass transition temperature T_g was not reached.

On the other hand Fig. 3(a) describe the behavior of polarization as a function of temperature according to the relation⁴

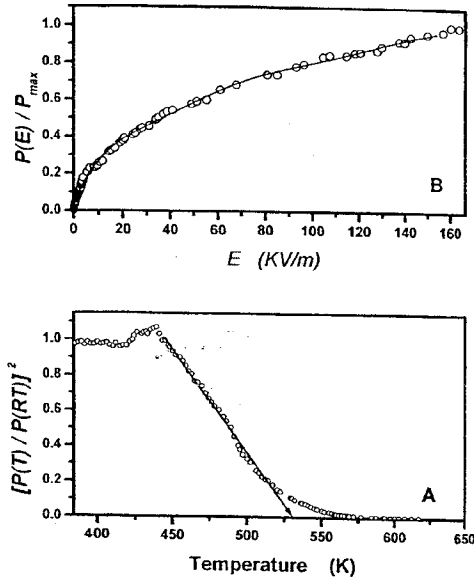


FIG. 3. (a) Reduced polarization as a function of temperature according to Eq. (2) of the as-quenched glass sample, showing the intersecting Curie's temperature with $P(RT)=0.23 \mu\text{C}/\text{cm}^2$. (b) Room temperature variation of the reduced polarization $[P(E)/P_{\text{max}}]$ as a function of the applied ac field at 70 Hz, as obtained using the Sawyer and Tower circuit (Ref. 15), with $P_{\text{max}}=0.26 \mu\text{C}/\text{cm}^2$.

$$\frac{P(T)}{P(RT)} = \left[\frac{T_c - T}{T_c} \right]^{1/2}, \quad (2)$$

where $P(RT)=0.23 \mu\text{C}/\text{cm}^2$ at room temperature, the straight curve intersects with temperature axis at the Curie temperature T_c , which is almost the same as obtained following the above techniques.

Figure 3(b) however, shows the room temperature variation of the reduced polarization with $P_{\text{max}}=0.26 \mu\text{C}/\text{cm}^2$, as a function of the applied ac field at 70 Hz. It can be seen that as the field is increased the corresponding polarization increases to saturate at much higher fields. A similar behavior characterizes clamped ferroelectric materials.²²

In conclusion it is evident that the as-quenched glass of the chemical composition $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_{1.2}\text{Ca}_2\text{Cu}_{2.8}\text{K}_{0.2}\text{O}_z$ prepared by the melt-quenching technique possibly shows clear ferroelectric properties. The Curie temperature at 530 K is lower than the glass-transition temperature, i.e., $T_c < T_g$, with no trace of crystallization. It was also found from the dielectric measurements that the transition (ferroelectric $\leftrightarrow$ paraelectric) is reversible if T_g is not reached. This indicates that the ferroelectric ordering may have an origin due to residual microstresses developed during quenching of the glass melt. However, ferroelectrics such as ours may be explained by the presence of dipole inhomogeneity. The inhomogeneity is either ascribed, first to the composition fluctuation, which is almost macroscopic in scale. Secondly to the fluctuation in chemical ordering, which is intermediate in length scale. And thirdly to glassy dipolar frustration of the microscopic (ferroelectric or antiferroelectric) ordering of ions whose scale is of the order of the glass network.

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