High Temperature Corrosion Research in Progress: 1997

(A through J)

TR-110333-V1

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REPORT SUMMARY

High-temperature oxidation and corrosion are important life-limiting factors for several critical components in thermal power systems. Research into many aspects of the problem is taking place in laboratories worldwide. This report, a survey of work in progress, updates and extends EPRI's 1994 report TR-104124, Volumes 1 and 2.

Background
Oxidation and corrosion are of major importance for gas turbine blades and vanes; gas coolers in coal gasification systems; superheaters, reheaters, and furnace wells in conventional boilers; in-bed tubes in fluidized-bed combustors; and, most components in high-temperature fuel cells. Problems of oxidation and corrosion are combated by the development and selection of materials resistant to the specific environment, including corrosion-resistant coating systems. Materials development is based on research aimed at understanding the mechanisms of various high-temperature oxidation and corrosion processes.

Objectives
To inform materials developers and materials selection engineers of research in progress relating to use of materials at high temperatures in aggressive environments.

Approach
The authors designed a questionnaire and sent it to laboratories engaged in high-temperature oxidation and corrosion studies and to others where such work was a possible development. The authors compiled the results of the questionnaires and circulated a draft to the same laboratories for corrections, amendments, and additions.

Results
Most key laboratories contacted responded in some detail. The report, thus, provides a relatively comprehensive picture of the state of ongoing research in high-temperature oxidation and corrosion studies.

EPRI Perspective
Comprehensive directories of work in progress in technical fields relevant to the electric utility industry are valuable in planning R&D. They are of great benefit when transferring basic research results to those concerned with materials and process development, to equipment designers, and, ultimately, to operators. They also provide a directory of experts in relevant areas. This particular directory should be valuable to anyone who uses materials at high temperatures in aggressive environments.

AP-110333

Interest Categories
Fluidized Bed Combustion
Fossil Steam Plant O&M Cost Reduction
Combustion Turbine/Combined Cycle Plants
Applied Science & Technology

Keywords
High-temperature materials
Oxidation
Corrosion
Metals
Alloys
Ceramics
Semiconductors
Intermetallics
Coatings

ACKNOWLEDGMENTS

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The information was collected, edited and assembled by Professor Graham C. Wood of the University of Manchester Institute of Science and Technology, Manchester, England; and Dr. John Stringer, of Materials Performance, Energy Conversion Division, EPRI.

FOREWORD

This report is a digest of replies to letters sent out from September 1996 onwards, or reminders sent out subsequently. The contributors were sent a first draft for correction in October 1997 of responses received throughout the year of the survey.

The opportunity has been taken not only to update the entries in the previous report on this subject, EPRI TR-104124-V1 and V2, but also to extend the survey to other laboratories. The scope has also been broadened to include more on work under nuclear steam temperature and pressurised hot water attack conditions, and on semiconductors, principally silicon. We have been greatly assisted in obtaining additional contacts by using the Survey of Corrosion Research Laboratories, prepared by Dr. R. J. Hussey of the National Research Council of Canada on behalf of the International Corrosion Council (ICC), lists of attendees at conferences and other similar sources.

There may be some duplication because, in a few cases, research sponsors or principal investigators have sent entries for all the investigators sponsored by the groups, while the individuals have sent in personal contributions, or have been mentioned in collaborative ventures between laboratories. We elected not to attempt to edit these excessively.

Despite our best efforts to be comprehensive, some research groups may not have been approached and, in certain cases, replies were not received even after several reminders. We regret any omissions resulting from this or other causes. We thank warmly those who have assisted us in obtaining responses in their countries, namely Professor Michael Graham (Canada), Professor Bernard Pieraggi (France), Professor Dr. Michael Schutze (Germany), Professor Francesco Gesmundo (Italy), Dr. Yosh Shida (Japan), Mr. Jim Norton (Netherlands), Professor Christofer Leygraf (Sweden) and Dr. Ian Wright (USA).

The report is for information only. No attempt has been made to comment on the research. The length of entries normally reflects the amount of material, within the context of the survey, provided by the investigators, and is not intended to indicate the relative importance of the work being undertaken in the various laboratories. The survey is arranged by country in alphabetical order and then by principal investigator, again in alphabetical order.

As in previous editions, the emphasis is on film or scale formation and breakdown on metals, alloys and ceramics. However, as already mentioned, the scope has been broadened to include important material on oxidation of silicon and other semiconductors. Likewise, there is an increased contribution under nuclear steam temperature and pressurised hot water attack conditions but, in that case, the emphasis is sometimes on stress corrosion cracking, intergranular corrosion, hydrogen uptake and allied subjects.

In just a few cases, in the interests of international cooperation, technology transfer, networking and completeness, we have included entries where work is either being phased out, or is just starting, or is even a little marginal to the main thrust of the Survey.

A large document like this is only really useful if it can be easily interrogated for information. As last time, we have not produced a subject index but rather two sets of keywords, one of scientific keywords and the other of keywords identifying areas of technology, served by the high temperature corrosion work reported. Principal investigators were able to select from menus in each category and were also able to suggest one or two keywords of their own. These keywords form the basis for the subject index.

As before, we have also prepared a name index. This is based on the principal investigator(s) listed and the names of collaborators in the initial headings, or the text. We have not used the listed publications in the preparation of either the subject index or the name index. We may prepare a separate list of publications for circulation in due course.

This time, the instructions to the participants were constructed to obtain a reasonably consistent format, whilst allowing the free rein that many contributors had requested in response to a questionnaire that we circulated quite widely prior to undertaking the survey. We are grateful to all those who responded to this prior questionnaire but particularly to our colleague, Dr. Ian Wright, of the Oak Ridge National Laboratory, who gave us much valuable advice and guidance in reaching a balance between freedom in individual contributions and ability to interrogate the information. A few entries which do not conform to the format proposed have nevertheless been included for completeness.

The report has been provided gratis in disk or CD ROM form to all principal investigator contributors. Hard copy versions have been provided to EPRI members and are available for purchase by others.

We would be interested in the views of readers as to the usefulness of a compilation of research in progress such as this.

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VOLUME 1

VOLUME 2

ARGENTINA

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Scientific Key Words:	Pitting; High temperature water corrosion; Electrochemical measurements; AC impedance measurements; Heat Exchanger materials
Technical Key Words:	Nuclear power systems; Steam generators.

SCOPE OF RESEARCH

Fundamental Approach

The general objective of the research is to evaluate the effect of different environmental parameters, such as temperature, potential and solution composition on passivity and localized passivity breakdown of nuclear steam generator tubing alloys in pressurized water cooled reactor (PWR and PHWR)systems. In order to accomplish this objective, electrochemical tests are being performed to investigate the anodic behavior of nuclear grade Alloy 800 in aqueous solutions of different electrolytes at temperatures ranging from 60°C to 280°C. The role of environmental variables on the morphology of the attack and the properties of the passive film has also been studied.

Applications, Engineering Achievements and Technology Transfer

Corrosion has been the major cause of tube failures in nuclear steam generators. Many of such problems have been attributed to the local concentration of water impurities in regions of restricted water access and overheating such as crevices or under scale. The main sources of impurities are in-leakages of cooling water containing dissolved impurities, corrosion products of the secondary circuit and resin particles or regenerants released by water purification devices Studies, such as these, of environmental factors involved in corrosion processes can provide valuable information to identify the environmental conditions in the degraded areas.and to control and mitigate corrosion problems in nuclear steam generators.

Specific Topics

1. The Effect of Temperature on the Passive Film Properties and Pitting Behavior of Alloy 800

The aim of the work is to investigate the relationship between the properties of the passive film and the localized corrosion behavior of Alloy 800 in high temperature aqueous solutions. The effect of temperature on the properties of the oxide films formed on Alloy 800 in 0.1M NaCl and 0.1M Na_2SO_4 aqueous solutions at temperatures up to 280°C was studied by *in situ* alternate current (AC) impedance spectroscopy. The results were compared with the passivity breakdown behavior and pitting morphology found for Alloy 800 in potentiodynamic polarization tests run under the same experimental conditions. The effect of temperature on the pitting potential and the pitting morphology of Alloy 800 in chloride solutions was found to be associated with a temperature-affected variation of the passive film porosity.

2. The Effect of Dissolved Impurities on the Corrosion Behavior of Alloy 800 in High Temperature Aqueous Solutions

A systematic study is being carried out into the influence of possible impurities on the corrosion behavior of Alloy 800. The aim is to define the role of individual species in the pitting susceptibility of the alloy.The anodic behavior and passivity breakdown of Alloy 800 in aqueous solutions of sodium chloride, sodium sulfate, sodium bicarbonate and sodium phosphate were studied by electrochemical techniques in the temperature range from 25°C to 280°C. The pitting resistance and pitting morphology of the alloy in chloride plus sulfate, chloride plus bicarbonate and chloride plus phosphate mixtures were also examined.

RECENT PUBLICATIONS

1. Olmedo, A.M., Villegas, M. and Alvarez, M.G., “Corrosion Behaviour of Alloy 800 in High Temperature Aqueous Solutions: Electrochemical Studies,” Journal of Nuclear Materials, 229, 102-114 (1996).

2. Carranza, R.M. and Alvarez, M.G., “The Effect of Temperature on the Passive Film Properties and Pitting Behaviour of a Fe-Cr-Ni Alloy,” Corrosion Science, 38, 909-925 (1996).

3. Alvarez, M.G., Olmedo, A.M. and Villegas, M., “Corrosion Behaviour of Alloy 800 in High Temperature Aqueous Solutions: Long Term Autoclave Studies,” Journal of Nuclear Materials, 229, 93-101 (1996).

AUSTRALIA

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Scientific Key Words: Multiphase alloys; Interdiffusion; Gas mixtures; Internal precipitation; Coatings; Intermetallics; Predictive capability; Thermal cycling; Gas-solid reaction kinetics

Technical Key Words: Petrochemical industry; Gas turbines; Combined cycle systems; Pyrolysis furnaces; Heat treatment; Reformers; Reheat furnaces

SCOPE OF RESEARCH

Fundamental Approach

The basic research program is centered around the diffusion and phase transformation processes associated with high-temperature corrosion reactions. Several projects are concerned with diffusion in growing scales and also in the coated and uncoated alloys undergoing reaction. In addition, the mass transfer processes occurring in complex and sometimes dilute gas mixtures are recognised as potentially contributing to reaction control. Examples of these latter reactions are also under study. Phase transformations in alloys can be important when selective reaction of alloy components occurs. The resulting changes in alloy subsurface composition and, as is often a consequence, phase assemblage, are being studied for a number of cases. These include dissolution of alloy precipitate phases, transformations of alloy intermetallic phases and internal precipitation of corrosion reaction products. A significant body of work is also concerned with corrosion in mixed gas atmospheres. This work is concerned with both external scaling and internal precipitation in gas mixtures which are oxidising-carburising, oxidising-sulfidising, oxidising-sulfidising-carburising and carburising-nitriding. Thermal cycling is used to accelerate reactions and make the alloy transformation and diffusion processes more readily accessible. A number of diffusion couple studies is also being carried out in support of the various gas-solid and solid-

solid interaction studies. The diffusion couple studies are relevant to interactions between the component phases in composites and to the understanding of complex diffusion paths developed in gas-alloy corrosion reactions and coating/substrate interdiffusion processes.

Applications, Engineering Achievements and Technology Transfer

Although most of the laboratory's work is concerned with fundamental studies, the unusually broad range of controlled gas atmosphere equipment is of particular value in simulating operating conditions encountered in the process industries. Examples include the carburising and metal dusting conditions found in some petrochemical and gas generation processes, the sulfidising-oxidising conditions produced in some combustion processes, carburising-nitriding conditions produced in heat-treatment operations, etc. Large scale collaborative projects have been carried out with three steel companies, two petrochemical companies, an aerospace company and an aluminium company. A large number of smaller collaborative investigations have also been completed.

Specific Topics

1. Studies in Multiphase Alloy Oxidation

Formation of a protective scale implies selective removal of a particular metal constituent from an alloy. Depletion of this element from the surface region of a multi-phase alloy can displace the composition in such a way that a different phase assemblage results. Three different systems are being studied. The dissolution of Ni_3Si precipitates in a matrix of γ-Ni is observed to accompany the formation of an external SiO_2 scale. A subsurface zone of precipitate dissolution forms during the formation of an external SiO_2 scale. The width of the subsurface zone increases parabolically with time. Diffusional analysis has shown that mass transfer is controlled by diffusion through the single-phase depletion zone, with Ni_3Si dissolution not contributing to rate control. The dissolution of chromium carbides in Fe-Cr-C alloys oxidising at 850°C is also being studied. Cast alloys containing coarse interdendritic $M_{23}C_6$ form fast-growing iron oxide scale rather than protective Cr_2O_3. When hot forged to yield carbides of about 1μm in size, the same alloys oxidise under the same conditions to form protective Cr_2O_3 scales. The effect of alloy matrix constitution is also being investigated by using alloy additions to control the γ - α equilibrium. As expected, alloys containing the high diffusivity α-phase form a Cr_2O_3 scale more readily. Oxidation-induced phase transformations in Ni-Cr-Al alloys are also being studied. The selective oxidation of aluminium during cyclic oxidation results in a destabilisation and subsequent phase transformation of the original α-Cr+β-NiAl structures to γ-Ni or γ-Ni +α-Cr. With continued cyclic oxidation, a further transformation of the $\alpha+\beta$ structure to $\gamma+\beta$ occurs.

This latter transformation is due to both aluminium depletion from and nickel enrichment into the $\alpha+\beta$ structure.

2. Complex Subsurface Precipitation in Alloys Exposed to High Temperature Gases

Although internal oxidation and other single component internal precipitation reactions have been extensively studied, very little information is available for the situation of practical interest where alloys are exposed to atmospheres containing more than one oxidant. Current work shows that distinct precipitation zones form during the internal corrosion of several commercial heat-resistant alloys in multi-oxidant gases (sulfidising-oxidising, sulfidising-carburising-oxidising and carburising-oxidising). The growth of individual zones follows parabolic kinetics as expected. However, the rates of zone growth are different from the corresponding rates in single oxidant gases. One clearly obvious interaction between oxidants is found in the case of carburising-nitriding of iron-nickel-chromium alloys. When carburised, these alloys form small blocky or spheroidal precipitates. When nitrided, they form lamellae or Witmanstatten precipitates. When first nitrided and then carburised, the alloys develop carbides with the morphologies of the first-formed nitrides. When subjected to simultaneous carburising and nitriding, the alloys develop zones of carbides with nitride-type morphologies, although no nitride can be detected within the precipitation region.

3. Temperature Cycling in Mixed Gases

Considerable information is available on the effects of thermal cycling during oxidation. However, little is known of the effects of thermal cycling during corrosion in mixed gases. This project involves the study of the effect on commercial heat-resistant alloys of exposure to alternate cycles of carburising-reducing conditions and oxidising conditions in the absence of carbon. Internal carburisation is always observed and the rate of this process measured with respect to cumulative carburisation time is found to obey parabolic kinetics. Accelerated rates were found as a result of “metal dusting” attack on the alloys and increased carbon activities in their surface regions. Work is now being extended to thermal cycling of alloys exposed to gas mixtures of CO/CO_2 which are strongly carburising and mildly oxidising.

4. Microstructural Degradation of Aluminide-Coated Nickel-Based Alloys During High-Temperature Exposure

The service life of the protective coatings at elevated temperatures becomes severely limited due to diffusive interactions between the coating layer and the component substrate. Knowledge of diffusive interactions is essential for the development of aluminide coatings capable of longer life and improved reliability. The purpose of this project is to characterise the microstructural changes which occur in aluminide-coated Ni-Cr-Al model alloys and commercial nickel-based superalloys during high-temperature exposure. The coating/substrate interdiffusional processes can be qualitatively explained using the concepts of diffusion paths applied to Ni-Cr-Al isotherms.

5. Thermodynamics and Kinetics of Interfacial Reactions in Intermetallic/Ceramic Composite Systems

Ceramic-reinforced intermetallic-matrix composites are attracting considerable attention because of their light weight and potential for high strength and stiffness at elevated temperatures. Quite surprisingly, however, virtually no studies have been published on the chemical compatibility of the various intermetallic/ceramic combinations when subjected to high-temperature oxidising environments. Such studies are necessary in order to optimise the design, fabrication and selection of future intermetallic composites. This project seeks to gain a better understanding of thermodynamics and kinetics of interfacial reactions in intermetallic/ceramic systems. Research has focused primarily on titanium-aluminide matrix composites reinforced with Al_2O_3. This has involved a detailed study to determine the stable and metastable phase equilibria in the Ti-Al-O system at 900-1100°C, together with a kinetic study using diffusion couples of Al_2O_3 with different titanium-aluminide based alloys.

6. Control of Scaling During Hot Processing of Steel

This project is in collaboration with a major Australian steel company. The secondary processing of steel involves heating the steel to high temperatures (up to 1300°C), followed by rolling it into shape and then cooling. During these operations the steel surface oxidises extensively. Much of the reaction product scale, representing ~2% of the product, is lost. The final product is covered by a millscale which controls the steel's short-term rust resistance and subsequent ease of cleaning. The focus of this project has been to determine the effects of changes in the temperature-time schedules and furnace atmospheres on scaling behaviour of various commercial steels. Optimal conditions for reducing scale losses, and controlling final scale properties are being identified.

7. Rapid SiO_2 Growth on Silicides and Silicide-Containing Alloy During Thermal Oxidation

The formation of a SiO_2 layer by the thermal oxidation of silicon and silicon-containing alloys is of considerable importance to the microelectronics and high-temperature materials industries. In spite of this, however, the mechanisms associated with SiO_2-layer formation are not well understood. This is partly due to the problem of identifying experimental methods that are more revealing of the SiO_2 growth behaviour. In this project, the anomalously wide range of SiO_2 growth kinetics on different silicides and silicide-containing alloys is utilised to gain a better and more unified understanding of SiO_2 growth. It is of particular interest to correlate and quantify the variation in SiO_2 structure with growth kinetics.

RECENT PUBLICATIONS

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2. Chen, Y., Young, D.J. and Blairs, S., "High Temperature Sulfidation Behaviour of Fe-Mo-Mn-Al Alloys," Oxidation of Metals, 40, 433-60 (1993).

3. Chen, Y., Young, D.J. and Blairs, S., "Effects of Manganese Additions on the Sulfidation Behaviour of an Fe-28Mo Alloy," Corrosion Science, 36, 401-14 (1994).

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5. Carter, P., Gleeson, B. and Young, D.J., "Calculations of Precipitate Dissolution Zone Kinetics in Oxidising Binary Two-Phase Alloys," Acta Materialia, 44, 4033-38 (1996).

2. Interdiffusion

6. Lee, C.W.M., Gleeson, B. and Crosky, A., "The Effects of Overheating on Aluminide Coated Rene 80H Turbine Blades," Proc. 5th Australian Aeronautical Conf., Inst. Eng., Aust., p369 (1993).

7. Young. D. J., "Diffusion in Solids," in Encyclopedia of Applied Physics, 18, 521-40, VCH Publishers, New York (1996).

3. Gas Mixtures

8. Zheng, X.G. and Young, D.J., "High Temperature Corrosion of Cr_2O_3-Forming Alloys in CO-CO_2 -N_2 Atmospheres," Oxidation of Metals, 42, 163-90 (1994).

9. Tjokro, K., Young, D.J., Johansson, R.E. and Ivarsson, B.G., "High Temperature Sulfidation-Oxidation of Stainless Steels," Journal de Physique IV, 3, 357-364 (1994).

10. Zheng, X.G. and Young, D.J., "High Temperature Corrosion of Pure Chromium in $CO-CO_2-SO_2-N_2$ Atmospheres," Corrosion Science, 36, 1999-2015 (1994).

11. Harper, M.A., Ducasse, M. and Young, D.J., "Cyclic Oxidation Plus Carburization of Heat-Resistant Alloys," Corrosion, 51, 191-200 (1995).

12. Young. D.J. and Watson, S., "High Temperature Corrosion in Mixed Gas Environments," Oxidation of Metals, 44, 239-64 (1995).

13. McAdam, G. and Young, D.J., "Mechanisms of Simultaneous Sulfidation and Oxidation of Fe-Mn Alloys," Corrosion Science, 34, 247-66 (1996).

4. Internal Precipitation

14. Tjokro, K. and Young, D.J., "Comparison of Internal Nitridation Reaction in Ammonia and in Nitrogen," Oxidation of Metals, 44, 453 (1995).

15. Young, D.J. and Watson, S., "Internal Corrosion of Engineering Alloys," Proc. 35th Annual Conf. Aust. Corros. Assoc., paper 31 (1995).

5. Coatings

16. Da Costa, W., Gleeson, B. and Young, D.J., "Co-Deposited Chromium-Aluminide Coatings: Part 1. Definition of the Co-Deposition Regimes," Journal of the Electrochemical Society, 141, 1464-71 (1994).

17. Da Costa, W., Gleeson, B. and Young. D.J., "Co-Deposited Chromium-Aluminide Coatings, Part II: Kinetics and Morphology of Coating Growth," Journal of the Electrochemical Society, 141, 2690-98 (1994).

18. Hadavi, S.M.M., Gleeson, B. and Young, D.J., "Sulfidation Behaviour of Silicide Coated 9Cr-1Mo Steel," Proc. 5th World Seminars on Heat Treatment and Surface Engineering, Iran, pp213-222 (1995).

BELGIUM

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Scientific Key Words: Thermodynamic stability diagrams; Thermodynamic modeling; Thermodynamics in oxides

SCOPE OF RESEARCH

An "Atlas of Chemical and Electrochemical Equlibria in the Presence of a Gas Phase" is being prepared. It is authored by Pourbaix, Marcel (Cebelcor), Zhang, Heming, and Yang, Xizhen (ShanDong University of Technology, Jinan, P.R. China).

Fundamental Approach

These equilibrium diagrams are of the two types E = f(T) and/or log r = f(1/T), where T is the temperature (in Kelvin), E the electrode potential versus a given reversible reference electrode (for instance an oxygen-, hydrogen- or chlorine-electrode), and p the partial pressure of a given gas (O_2, H_2 or Cl_2). Both these two types of diagrams show the influence of temperature and pressure on the conditions of stability and metastability of <u>all</u> substances (solid, liquid and gaseous) likely to occur in a given chemical or electrochemical system (with 1, 2, 3 or eventually 4 components). These diagrams may also show, for non-equilibrium conditions, the affinities of the reactions and, sometimes, kinetic information (catalytic action, exchange currents and velocities of reactions). A walk along the lines of these diagrams may, at any step, lead to the confirmation and explanation of facts already known, or to the detection of errors or gaps in the existing literature, or to the discovery of unknown facts, which may sometimes be important. These diagrams may be particularly helpful as a guide for the study of all processes occurring at high temperature, and this, not only for processes involving a gaseous phase, but also for processes involving an electrolyte (such as water or a molten salt) or a solid solution (such as non-stoichiometric oxide or sulfide).

Eventually, the Atlases will cover all elements of the periodical system (one-component systems), and the oxides, hydrides, carbides, chlorides, fluorides, sulfides, hydrates, carbonates and sulphates of these elements (two-component systems). Some three component systems of particular interest will also be considered. As such, they will be useful as text-books for teaching and research in fundamental inorganic chemistry and electrochemistry, and in numerous applications such as industrial chemistry, electrolysis, ferrous and non-ferrous metallurgy, electrometallurgy, batteries and fuel cells, catalysis, geology, and corrosion.

Part I of this new Atlas was published in 1996, with the following content:

Introduction

One-element systems: O, H, Fe, Cl, S

Two-element systems: O-H, O-Fe, O-Cl, H-Cl, X-S, O-S, S-Fe

Three-element systems: O-Cl-H, O-S-Fe

Four element systems: O-Cl-H-Fe

Part II of the new Atlas is under preparation and is due to be published later in 1996 or early 1997. Its content is:

One-element systems: C, Al, Cr, Si, Nb

Two-element systems: O-C, O-Al, O-Cr, O-Si, O-Nb, S-Cr, C-Si

Three-element systems: O-H-Fe, O-C-Fe, O-C-Al, O-S-Cr, O-C-Si

It is intended to cover all combinations of elements that are of scientific or practical interest. The task is huge. Therefore, teams that are interested in this work, or industries and organizations that have an interest in specific systems are invited to contact Cebelcor.

Related publications were included in the 1991 EPRI survey on this subject.

RECENT PUBLICATIONS

1. Pourbaix, M., Zhang, Heming and Yang, XiZhen, “Atlas of Chemical and Electrochemical Equilibria in the Presence of a Gaseous Phase,” CEBELCOR, Brussels, Eds. Heming Zhang, and A. Pourbaix, (1996).

BRAZIL

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Scientific Key Words:	Oxidation; Sulfidation; Oxidation at low oxygen pressure; Refractory metals; Fe-Nb alloys; Fe-Ta alloys; Aluminum alloys; Gas mixtures; Maraging steel
Technical Key Words:	Aluminum recycling; Combustion gases; Fossil fuel-fired boiler; Oxidation in heat-treatment

SCOPE OF RESEARCH

Fundamental Approach

The involvement with high temperature corrosion research at the Department of Metallurgical and Materials Engineering is very recent and the Oxidation Laboratory has just been installed. The main initial objective is to investigate the oxidation kinetic behavior of different metals and alloys in different atmospheres. To accomplish this, two thermogravimetric balances and a complete set-up for handling and mixing gases have been installed. Moreover, the microstructural changes will be followed with optical and scanning electron microscopy and the identification of different components will be accomplished with microprobe and x-ray diffraction analysis.

Applications, Engineering Achievements and Technology Transfer

The main objective is to develop alloys for application in fossil fuel-fired boilers using reducing atmospheres so as to lower the polluting gas emissions. Another area is that of aluminum cans recycling, in which the oxidation behavior of aluminum alloys during the melting procedure is evaluated. The oxidation of maraging steels during their heat treatment at high temperatures is also of concern.

Specific Topics

1. High Temperature Oxidation Behavior of Fe-Nb and Fe-Ta Alloys

In this research the oxidation behavior of Fe-Nb and Fe-Ta alloys is investigated in atmospheres with low oxygen and medium sulfur content, aiming at their possible application in fossil fuel-fired boilers using reducing atmospheres so as to lower the polluting gas emissions. This research is supported by FAPESP (São Paulo State Foundation for Support of Research).

2. Oxidation Behavior of Aluminum Alloys Used in Can Manufacture

In this research the oxidation behavior of aluminum alloys AA5182 and AA3004, used in can manufacture, is investigated. The aim is to determine the best melting conditions of aluminum cans with the lowest weight loss of metallic aluminum. This research is partially supported by FAPESP (São Paulo State Foundation for Support of Research).

3. High Temperature Oxidation of High Molybdenum Maraging Steels

In this research the high temperature oxidation of high molybdenum maraging steels is investigated in order to understand better their behavior during their heat treatment at temperatures higher than 1200ºC. This research is supported by FINEP (Brazilian Federal Agency for Financial Support of Studies and Projects).

RECENT PUBLICATIONS

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CANADA

CONTENTS

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Material Degradation

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Scientific Key Words: Corrosion; Erosion; Plasma coatings; Thermal cycling; Superalloys; Reducing environments; Molten salts; Gas mixtures; Oxidation

Technical Key Words: Coal gasification; Syngas coolers; Fossil fuel-fired boiler; Heat exchangers

SCOPE OF THE RESEARCH

Fundamental Approach

The research is focused on the mechanisms of scale formation and its role in the protection of alloys and coatings in reducing environments. The research includes fundamental studies of multi layered scale formation and the diffusion processes within these layers/scales in mixed gas atmospheres. Examples include coal gasification, or low NOx boiler environments, where sulfur, carbon, or chlorine potentials are high and oxygen potentials are low and fluidized-bed coal combustion, or oil catalytic cracking conditions, where materials degradation is caused by impact erosion of solid particles. The effectiveness of metallic, intermetallic, ceramics and composite coatings for protection has been studied.

Applications, Engineering Achievements and Technology Transfer

The Canada Centre for Mineral and Energy Technology (CANMET) is mainly conducting applied research for the mining and energy industry. The high-temperature corrosion research activity is mainly concerned with the energy conversion industry, such as coal-fired boilers, coal gasifiers and fluidized bed combustors. The work is often undertaken in conjunction with consortia of industrial partners, or single sponsors or is fully funded by the Canadian Government. The following are current research projects in the field of High-Temperature Corrosion at the Materials Technology Laboratory of CANMET.

Specific Topics

1. Alloys and Thermal Spray Coatings for Coal-Fired Low NO_x Boilers

This research is being carried out in collaboration with a number of Canadian Utility companies, Canadian Electricity Association and two CANMET laboratories, the Energy Research Laboratory (ERL) and the Materials Technology Laboratory (MTL). The overall aim of the work is to investigate the application of thermal spray coatings on existing water wall materials of fossil fuel-fired boilers operating under low NOx conditions. Emphasis is being placed on the effect of coating composition on the mechanism of scale growth and its resistance to spallation with and without slag deposition. In addition to the gas sampling from an actual power plant, results obtained from pilot-plant studies at ERL are being used in laboratory corrosion and erosion tests at MTL to closely simulate low NOx conditions.

2. The Effect of Minor Alloying Elements on the Hot Corrosion of Ni-Cr Alloys

The aim of this work is optimize alloy composition in order to minimize metal wastage when the alloy is used in chemical recovery boilers. Optimization of the alloy composition is being made to suit the operating temperatures. The effects of the minor alloying elements and the velocity of the smelt on the rate of metal wastage are also being studied.

3. Materials for Syngas Cooler

The aim is to obtain a better understanding of material performance in highly reducing atmospheres at a wide range of temperatures. Emphasis is being placed on the formation of protective scales on superalloys and thermal spray coatings at high potentials of sulfur and low potentials of oxygen. The important material and environmental parameters which influence corrosion and erosion behavior are being assessed.

4. Scale Formation and Removal During Steel Reheat

This research includes two parts. The first part is focused on the effect of residual elements in reducing the thickness of the oxide scale that will usually develop on the steel during reheat process. The second part is focused on developing a new technique to facilitate the removal of the thin oxide scale after reheat process and before rolling process.

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Scientific Key Words:	Superalloys; Overlay coatings; Thermal barrier coatings; Interdiffusion; Life assessment
Technical Key Words:	Gas turbines; Thermal barrier coating systems; Conventionally- cast alloys; Directionally-solidified alloys; Single crystal alloys

SCOPE OF RESEARCH

Fundamental Approach

The overall goal of this work is to develop improved techniques for life assessment and life prediction of gas turbine hot section components. A critical aspect of component life is the durability and performance of high temperature protective coatings. The degradation of these coatings may take place by oxidation, hot corrosion, fatigue cracking and interdiffusion with the nickel and cobalt-base superalloy substrates. The actual mechanisms and kinetics of degradation are dependent on the specific operating conditions which vary from application to application. In particular, the component temperature distributions are one of the least predictible unknowns, although they are undoubtably one of the most important factors affecting coating life. A program is underway to evaluate the kinetics of coating degradation via interdiffusion with nickel and cobalt-base superalloy substrates.

Applications, Engineering Achievements and Technology Transfer

The company provides a variety of engineering services, including component life assessment, to gas turbine users worldwide. Applications include gas turbines used by electric utilities, combined cycle plants and the petrochemical industry. The approach to component life assessment is interdisciplinary and involves both metallurgical and mechanical analysis to determine the modes of degradation and the potential for continued safe service. The metallurgical analysis looks for service-related degradation such as high temperature oxidation, hot corrosion and other changes in the base alloy microstructure which may affect the material properties. The mechanical analysis involves finite element computer modeling to evaluate heat transfer, stress and vibration.

Specific Topics

1. Development of a Surface Temperature Estimation Technique Based on the Beta Phase Depletion Rate of MCrAlY Coatings

This project is being co-sponsored by Wilson & Daleo Inc. and the National Research Council Canada through the Industrial Research Assistance Program. The goal of the work is to develop an alternative metallurgical temperature estimation technique for service-exposed hot section components based on the kinetics of interdiffusion between MCrAlY overlay coatings and nickel and cobalt-based substrates. The metallurgical temperature estimates can be used to calibrate finite element heat transfer models. A method based on overlay coating degradation would prove to be particularly useful in the case of cobalt-based substrate alloys, since no quantitative metallurgical temperature estimation technique currently exists for these alloys. Coatings of interest are the (Ni,Co)CrAlY overlay types which are used either in 'stand-alone' form, as thermal barrier bond coat layers, or those which are over-aluminized for increased oxidation protection. Collaborative ventures with gas turbine users on components and materials of specific interest are welcomed.

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2. Ellison, K.A., Daleo, J., and Boone, D.H., "Interdiffusion Between MCrAlY Coatings and $\gamma+\gamma'$ Ni-base Superalloys at 850°C," to be published in 1998.

3. Ellison, K.A., Daleo, J., and Boone, D.H., "Metallurgical Temperature Estimates Based on Interdiffusion Between CoCrAlY Overlay Coatings and a Directionally Solidified, Nickel-Base Superalloy Substrate," to be presented at the 6th Liege

Conference on Materials for Advanced Power Engineering, 5-7 October 1998, Liege, Belgium.

2. *Gas Turbine Component Life Analysis*

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Scientific Key Words:	Zirconium alloy corrosion; High temperature water corrosion; ZrO_2 dissolution; Hydrogen absorption; Intermetallics; Fluoride; LiOH
Technical Key Words:	Nuclear power systems; Fuel cladding behavior; Pressure tube lifetime

SCOPE OF RESEARCH

Fundamental Approach

As the lifetime of nuclear fuel cladding and CANDU reactor pressure tubes increases the limitations placed on the zirconium alloy tubes as a result of their corrosion, and the hydrogen that is absorbed concomitantly, are being reached or exceeded. Factors that are involved in reaching these limits have been increased fuel burnup (in order to obtain the maximum energy from the ^{235}U fissile components of the fuel); increased water outlet temperatures (to improve the efficiency of the reactor steam cycle) and increased power densities (to maximise the power output from a given size of reactor core). The consequences have been major development programs worldwide that are aimed at producing improved zirconium alloy fuel cladding and improved properties for Zr-2.5%Nb pressure tubes in CANDU reactors in order to extend their lifetimes. The ultimate aim of these programs is to produce alloys with lower corrosion and hydrogen absorption rates. However, development has had to be based on ad hoc approaches because the micromechanisms controlling corrosion and hydrogen absorption in-reactor are not understood. It is the aim of the research at the Centre for Nuclear Engineering to clarify these micromechanisms through fundamental studies of the properties of the oxide films formed in high temperature water and steam. In particular, the precise location and form of the alloying element atoms after the oxidation of the zirconium matrix, and the routes by which hydrogen is transported through the oxides are important. The presence of intermetallic particles in the original alloy, and chemical species such as LiOH and H_3BO_3 (added to the reactor water) and ^{19}F (generated by neutron capture in ^{18}O) are the keys to unlocking the required micromechanisms.

Applications, Engineering Achievements and Technology Transfer

It has been shown that LiOH is the key aqueous species in the degradation of the protective oxide films on zirconium alloys in nuclear reactors cooled by high temperature water. At high concentrations it has been found that LiOH preferentially dissolves the tetragonal form of ZrO_2 in the oxide film and redeposits a non-protective, porous monoclinic-ZrO_2 form. The process generates small interconnected pores because of the small size of the t-ZrO_2 crystallites. Although LiOH is only added at the 2-4 ppm (Li) level in the reactor water, high concentrations can be generated in the oxide film on the Zircaloy fuel cladding because of the high heat flux through the oxide and the fact that bulk water temperatures in recent PWRs can reach or exceed the saturation temperature at the cladding surface. Boric acid, added to control the reactor core reactivity, protects against such LiOH attack by precipitating a complex borate salt that plugs the pores. However, the boric acid concentration is reduced to zero at the end of each fuel cycle. Recommendations have been made to nuclear reactor vendors for changes in the way the water chemistry is controlled during reactor operation in order to minimise such effects, and the sensitivity of new zirconium alloys to various LiOH/H_3BO_3 combinations is being examined. ^{19}F, produced by neutron capture in ^{18}O, appears to have a synergistic effect on the ZrO_2 dissolution steps, if it is strongly absorbed by the oxide film. This absorption seems to be influenced by other components of the reactor water chemistry, such as the presence of dissolved hydrogen or oxygen. Some of these ideas will be tested in a collaborative program with the International Atomic Energy Agency, Vienna, and the Nuclear Research Institute at Rez in the Czech Republic. Nuclear reactors developed in the former USSR have always used different water chemistries from those designed in the West and the forthcoming start up of Temelin-1 (Czech. Rep.), with a Westinghouse first core, will provide an interesting test of these ideas. The importance of the intermetallics in the Zircaloys appears to derive from their local effect on the proportion of t-ZrO_2 in the oxide film and its influence on the ZrO_2 dissolution component of the oxide breakdown process. The intermetallics also have a local impact on hydrogen absorption processes that may derive from the formation of small local regions of iron oxides within the ZrO_2 film. These appear to be more readily soluble in reactor coolant than the ZrO_2.

Individual components of the program are described in the following abstracts:

Specific Topics

1. Effect of LiOH and H_3BO_3 on ZrO_2 Degradation

This research was carried out by Wu, Chenguang, who demonstrated the basic ZrO_2 dissolution and reprecipitation processes that form the key part of the mechanism. Further detailed TEM studies to locate Li and B in the oxide microstructure are in progress. In collaboration with Siemens and Framatome, evidence for the interaction of LiOH and H_3BO_3 concentration changes in reactor water with the corrosion behavior of the fuel cladding are being sought. However, the number of variables that can change in-reactor from one fuel cycle to the next make it difficult to obtain definitive evidence for such effects.

2. Synergistic Effects of LiOH and F^-

Fluoride ion in the high temperature water is the only other species besides LiOH that causes severe degradation of oxide films on zirconium alloys. Studies of the mechanism by which fluoride ion degrades the oxide suggest that it is very similar to the mechanism observed in concentrated LiOH, that is a hydrothermal dissolution and redeposition process with the oxide. Experiments have shown that synergistic effects occur if both LiOH and F^- are present, especially in water with a hydrogen overpressure. This is typical of conditions in PWRs where LiOH is added to control pH; dissolved hydrogen is added to suppress water radiolysis; and ^{19}F is generated by neutron capture in ^{18}O. This research is being carried out by Wong, Yin-Mei.

3. Color Centres in ZrO_2 Films

ZrO_2 films show strong fluorescence, thermoluminescence and cathodoluminescence. The effects that the alloying elements and strongly fluorescing impurities have on the various luminescence spectra are being studied by Yueh, Ken, for his Ph.D topic. Spectral peaks appear to be primarily intrinsic and only peak intensities and not positions are affected by changes in alloying elements and impurities.

4. Location of Alloying Elements in ZrO_2 Films

The precise locations of the alloying elements in the oxide film are not known. In the metal phase, elements like Cr, Fe and Ni are nearly insoluble in zirconium and occur as intermetallic particles. When the metal oxidises, so do the intermetallic particles. However, the fate of the alloying additions is not well known. The concentration of Fe, Cr and Ni in the intermetallic particles is well above the solubility of these elements in ZrO_2, so the question of whether the excess forms particles of transition metal oxides, or becomes distributed along the ZrO_2 crystallite boundaries is important to an understanding of the oxidation process. The small scale of the ZrO_2 crystallites (5-20nm in the oxides) makes it difficult to answer the above question. Using the Jeol 2010F at McMaster University, Sheikh, Haroon has been studying alloying element distribution for his M.A.Sc. project, and will probably be continuing with this for a Ph.D.

5. Hydrogen Uptake Mechanisms

The mechanisms by which hydrogen enters the zirconium during corrosion in high temperature water or steam is even less known that the detailed micromechanisms involved in the oxidation process. It is apparently not just a simple case of hydrogen atoms diffusing through the ZrO_2 film. Previous work has strongly indicated a very localised hydrogen absorption process, and it is suspected that it is associated with the intermetallic particles in the oxide (based on largely circumstantial evidence). Efforts to measure the hydrogen diffusional properties of intermetallic phases are currently being made by Esayed, Adel, a post-doctoral fellow. Use of both amorphous and crystalline intermetallics is involved because of the amorphisation of the intermetallics in the Zircaloys that occurs under irradiation. An additional study of the oxide breakdown that occurs when oxidised zirconium alloys are exposed to hydrogen gas (with a low oxygen partial pressure) is presently in suspension, but will be reactivated soon.

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4. Cox, B., "A New Model for the In-Reactor Corrosion of Zirconium Alloys," Int. Atomic Energy Agency, Tech. Comm. Meeting on Influence of Water Chemistry on Fuel Cladding Behaviour, Rez, Czech Rep. (1993).
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Scientific Key Words: Alumina growth; Mechanisms; Silicon oxidation; Reactive element effect; Secondary ion mass spectroscopy; X-ray photoelectron spectroscopy.

SCOPE OF RESEARCH

The objective of the research is to gain an increased understanding of the mechanisms of oxide growth on metals and semiconductors at high temperature. The research includes fundamental studies of the extent of oxygen diffusion in high temperature oxides and the role of 'reactive elements', such as cerium, in modifying growth processes.

Specific Topics

1. Mechanism of Growth of Alumina Scales

Collaborators: Mitchell, D.F., Prescott, R., Doychak J. (NASA Lewis), Lambertin, M., Béranger, G. (Université de Technologie de Compiègne, France), Jedlinski, J. (Jagellonian University, Poland), Schumann, E., Mennicke, C., Yang, J.C., Rühle, M. (Max-Planck-Institut für Metallforschung, Stuttgart, Germany).

The overall aim of this work is to obtain a better understanding of the mechanism of growth of alumina on β-NiAl and FeCrAl alloys (with and without zirconium or yttrium additions). The main techniques employed are high resolution SIMS imaging and depth profiling to follow oxide growth processes, and STEM/EDS to determine possible segregation of yttrium or zirconium to oxide grain boundaries and/or to the oxide/metal interface. The data illustrate the complexity of alumina growth.

2. *Growth and Transport in Thermal Oxide Films Formed on Silicon*

Collaborators: Tao, Y., Lu, Z.H., Tay, S.P. (AG Associates, San Jose), Jiang, D.T., Tan, K.H. (Synchrotron Radiation Center, Wisconsin), Cao, R., Pianetta, P. (Stanford Synchrotron Radiation Laboratory).

The research involves the growth and transport in oxide films formed on (100)Si at high temperatures. SIMS data and information from synchrotron photoemission spectroscopy (PES), complemented by X-ray photoelectron spectroscopy (XPS), are providing new insights into the oxide growth mechanism, interface suboxide structures, and the distribution of nitrogen in oxynitride films.

3. *Role of 'Reactive Elements' in Scale Growth on Chromia-Forming Alloys, Nickel and Other Metals*

Collaborators: Czerwinski, F. (McGill University), Rapp, R.A., Strawbridge, A. (Ohio State University).

This project is an investigation of the role of reactive elements in modifying oxide growth processes. Thin reactive element coatings are found to change the oxide growth mechanism of chromia and nickel oxide scales. Also, SIMS analysis of oxidized cobalt, iron and copper coated with alkaline earths show that some of the alkaline earth is present at the metal/scale interface, which would lend support to the 'poisoned interface model' explanation of the reactive element effect.

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4. General

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Scientific Key Words:	Aluminide alloying/coating; Burner rigs; Ceramics; Oxidation/sulfidation; Nickel alloys; Nickel oxidation; Stainless steels; Ceria coatings; Internal oxidation; Sulfur dioxide-oxygen attack; Ceramics corrosion; Ceramics/molten aluminium
Technical Key Words:	Sulphuric acid hot gas converter; Coal gasification; Combined cycle system; Heat Exchangers; Catalyst support systems; Ceramic components; Gas turbines;

SCOPE OF RESEARCH

Fundamental Approach

A series of fundamental studies on the development of protective oxide films and CeO_2 coating on nickel, nickel-aluminium and nickel-aluminium-silicon alloys and intermetallics in oxygen atmospheres has now been completed. Models have also been advanced for internal oxidation of these alloys. High temperature corrosion of silicon-based ceramics in combustion atmospheres is also studied. A newly initiated programme seeks to obtain an understanding of the behavior of stainless steels in oxygen-sulfur dioxide-sulfur trioxide environments at temperatures up to 650°C.

Applications, Engineering Achievements and Technology Transfer

A consortium of companies involved in the manufacture of sulfuric acid from metallurgical smelting operations is contributing to a program to test the behavior of a range of steels in the acid plant hot gas converter.

RECENT PUBLICATIONS

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3. Internal Oxidation

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4. Corrosion of Ceramics in Combustion Atmospheres

14. G-Ahari, K., Coley, K.S., Baxter, D. and Hendry, A., "Behavior of Sialons and Silicon Nitride in Burner Rig Simulated Gas Turbine Atmospheres," Proc. Conf. "The 8th CIMTEC World Ceramic Congress and Forum on New Materials, June 29-July 4, 1994. Advances in Science and Technology 9: High Performance Materials in Engine Technology, Ed. P. Vincenzini, Techna Publications, 411-420 (1995).

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Technical Key Words: Pulp/paper boilers; Waste-fired boiler; Furnace wall corrosion; Boiler tube failures

SCOPE OF RESEARCH

Fundamental Approach

The aims of the high-temperature corrosion research projects at Paprican are to limit the costly fireside corrosion problems currently being experienced in the Canadian Pulp and Paper Industry. The majority of the corrosion occurs in the lower furnace area of the recovery boilers, but there are also instances of corrosion in power boilers, particularly in the superheaters and generating banks. Several mechanisms of degradation are encountered, including sulfidation, molten salt attack, chloridation and erosion.

Applications, Engineering Achievements and Technology Transfer

In some cases, the research involves laboratory testing in furnaces and controlled atmospheres. On other occasions, special probes are inserted into boilers to expose corrosion coupons, collect deposits or detect molten salts. Sometimes boiler inspection or failure analysis is necessary.

Solution to fireside corrosion problems may involve advice on materials selection or changes in boiler operating conditions. More advanced long-term goals are to be involved in the development of improved materials, modifications to boiler design and the introduction of new technologies for corrosion monitoring.

Much of the work is undertaken with the cooperation of Paprican's Member Companies. Some projects are being carried out in conjunction with other research groups as indicated in the following abstracts which outline the major research projects underway in 1996.

Specific Topics

1. The Development of Materials for Service in Black Liquor Recovery Boilers

It was once thought that the solution to corrosion problems in the lower furnace of a kraft recovery boiler was the use of composite, or co-extruded tubes with an outer layer of 304L stainless steel. In recent years it has been found that such tubes are susceptible to cracking when used in floors and port openings. The overall aims of this research are to identify the cause of the cracking and to develop an improved material for furnace tubes. The work is being carried out in partnership with Oak Ridge National Laboratory.

2. Corrosivity Monitoring in Kraft Recovery Boilers

Previous work on this project has been directed towards the testing and evaluation of metallic materials and coatings for water-wall service in recovery boilers. In the present phase of the work, efforts are being directed towards monitoring corrosion in a sulfidizing atmosphere. this research is a joint endeavour with the Institute of Paper Science and Technology. Support is provided by the American Forest and Paper Association and the DOE.

3. Salt-Induced Corrosion in Coastal Power Boilers

Most power boilers are fired on waste wood consisting largely of bark. At a number of coastal mills, the bark comes from logs which were once stored and transported in sea water. Sodium chloride is present in the fuel and research has shown that it can give rise to problems such as fouling, intergranular corrosion and sootblower erosion in the superheater or generating bank.

RECENT PUBLICATIONS

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Scientific Key Words: Surface modification; Coatings; Computer modeling; Reactive element effect; Nickel oxidation; Zirconium alloys

Technical Key Words: Surface engineering; Nuclear power systems

SCOPE OF RESEARCH

General Description

The research of the Textures and Microstructures Laboratory at McGill University is focused on understanding the links between the processing of polycrystalline materials, their structure and their physical and mechanical properties. There is interest in the development and experimental verification of mathematical models which are used to simulate recrystallization, deformation, electrodeposition, high temperature oxidation and hydrogen permeation. In this scope, the research related to the high temperature oxidation is described.

Specific Topics

1. The Influence of Reactive Element Additions on the Oxidation of Metals and Alloys

The essential part of this study was conducted using Ni-NiO as a model system of cation-diffusing oxides, and Ce as a typical reactive element. Three techniques were employed to modify the surface of Ni with Ce and CeO_2: ion implantation, sol-gel technology and reactive sputtering. The improvement of Ni oxidation resistance was assessed by oxygen uptake measurements mainly during the early stages but also for long-term exposures at temperatures between 873 and 1073 K in pure oxygen. The various oxides produced were examined in detail by several advanced techniques, including RBS, AES, SIMS, TEM, STEM, AFM and X-ray diffraction. All the microstructural and texture results were explored to describe the transport properties of the CeO_2 modified NiO. In addition to Ni, CeO_2 coatings on pure Cr, steel, Ti and Inconel alloys were tested. This research was initiated at McMaster University (Hamilton, Ontario) with Smeltzer, W.W., Prof. The oxygen isotope experiments were performed in collaboration with Graham, M.J., Prof., from National Research Council in Ottawa (Ontario).

2. Model of Hydrogen Ingress in Zr-Nb Pressure Tubes

This research is being carried out in collaboration with Ontario Hydro Technologies (Toronto). The overall aim of the work is to build an atomistic mesoscopic model of hydrogen ingress through oxide films in Zr-Nb alloys and to test this model in various experimental conditions. This model will be used to predict the hydrogen ingress in pressure tubes used in nuclear power stations.

RECENT PUBLICATIONS

(Papers 1,2,3,4,8 were prepared at McMaster University, Hamilton, Ontario)

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SCOPE OF RESEARCH

Fundamental Approach

Dr. Tapping and his colleagues undertake nuclear-related R&D at reactor operating conditions; namely 300°C water. Some specifics are as follows:

1. Zr alloy corrosion in 300°C water as a function of material, water chemistry, flux and temperature. The contact here is Urbanic, V.F. There is also some separate work on fuel cladding, although not much on corrosion. Cox, D.S., is the contact.

2. Steam generator materials corrosion in 250°C to 300°C water is measured as a function of chemistry, heat flux, material and temperature. Materials studied are carbon steel, alloys 600, 690, 800. The contact is Gendron, T.S.

3. Carbon steel FAC in 300°C water is investigated as a function of chemistry, flux (radiation), temperature, and alloy additions. The contact here is Cheluget, E.

4. Water chemistry/thermodynamics at 300°C are investigated as support for the corrosion and fouling programs. The contact here is Balakrishnan, P.V.

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Scientific Key Words: Superalloy; Aluminide coatings; High temperature corrosion; Thermal barrier coatings; Diffusion barrier

SCOPE OF RESEARCH

Specific Topics

1. High Temperature Corrosion of Superalloys

The resistance and the corrosion mechanisms of superalloys used for gas turbines have been studied. Of special interest are the directionally solidified and monocrystalline alloys. The effects of grain boundaries, composition, heat treatments, and corrosive media on the corrosion resistance of superalloys is being investigated. Results are evaluated with gravimetry, metallography, and surface microanalyses. The primary aims of the research are to expand our knowledge of basic mechanisms of high temperature corrosion and, on the other hand, to develop more corrosion-resistant superalloys.

2. Modified Aluminide Coatings

Systematic experiments on the development of protective coatings against high temperature corrosion for nickel- and cobalt-based superalloys are conducted. The main work covers the preparation of coatings, which include Ti-Al, Si-Al, RE-Al, Pt-Al and Pd-Al coatings; the failure analyses of coatings under practical and synthetic aggressive environments; the effect of additive element such as Si, Ti, RE, Pt and Pd on corrosion resistant properties; the influence of coatings on the mechanical properties of substrates. Some of the coatings evaluated in both laboratory and field tests have been proved to be of practical importance.

3. Diffusion Barrier Coatings

The interdiffusion between an aluminide coating and the substrate significantly decreases the coating life above 1100°C. This problem may be solved if a barrier could be formed between the coating and the substrate. In this work, a metal-oxide layer, which was prepared by LPPS, has been tried for use as a barrier. The effect of the volume fraction of oxides, and the post-aluminizing treatment, on the effectiveness of the barrier has been investigated. It is proposed that the effectiveness of the diffusion barrier is decided mainly by (1) the volume fraction of oxides in the barrier, and (2) the ratio of volume-diffusion flux to short-circuit diffusion flux, A model calculaiton is established which is in agreement with the experimental results.

4. Gradient Thermal Barrier Coatings

This is a fundamental study of mechanical and physical properties of gradient TBCs. The gradient TBCs were prepared by plasma spraying in reducing atmospheres, or by sintering at high temperature and high pressure. The properties of the coatings, such as elastic and shear moduli, energy, nominal and tangential hardness, friction coefficient, expansion coefficient, and thermal conductivity, are being investigated. Analytical models of the relationship between the properties and structures of TBCs has been established.

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SCOPE OF RESEARCH

Specific Topics

1. A Novel Method to Measure the Oxidation Kinetics of Metals and Alloys

A new device to measure the oxidation kinetics of metals and alloys has been invented. This novel method is based on the theory of solid electrochemistry. In this device, the specimen is put into a sealed system composed of a yttria stabilized zirconium oxide tube with one end closed and a quartz tube with one end sealed, under a constant oxygen pressure. The yttria stabilized zirconium oxide tube coated with Pt at both the inside and the outside surfaces works at its most suitable temperature as an electrochemical oxygen pump. The quartz tube works at any temperature for the oxidation of metals and alloys. During oxidation, the amount of oxygen consumed by the oxidation of a specimen can be compensated by the electrochemical oxygen pump. All systems are controlled by a computer. It has been proved that the novel method can measure the oxidation kinetics of metals and alloys over a wide range of oxygen pressure as well as temperature. This device shows the prospect of replacing the electronic thermal balance for its higher accuracy to an extent.

2. The Diagram of Standard Free Energy for Unit Volume Oxide Formation

A new parameter EMBED Equation, standard free energy for unit volume oxide formation of metals, was introduced to analyze the nucleation abilities of oxides on metals thermodynamically. The EMBED Equation -T diagram for some oxides was established. From this diagram, the ability for metal oxides to nucleate at high temperature should be in the order of Al_2O_3 > MgO > HfO_2 > ThO_2 > CeO_2 > Y_2O_3 > CaO > Cr_2O_3 > Fe_2O_3 > ZnO > FeO > CoO > NiO. This order is quite different from that in Ellingham diagram. Therefore, the reactive elements would be selectively oxidized to form oxide nuclei in the Cr_2O_3-forming alloys, and promoting the formation of external Cr_2O_3 scales, but not in the Al_2O_3 forming alloys. This also implies that the free energy change per unit volume of oxide formation is a better criterion than the general free energy change of oxide formation in comparing the selective oxidation tendencies of alloying elements.

3. The Influence of Thin Surface Applied-Oxide Films on the Oxidation of Alloys

The effects of thin surface applied Y_2O_3, Cr_2O_3, Al_2O_3, Al_2O_3-Y_2O_3 films on the oxidation behavior of Ni-Cr, Fe-Cr, Fe-Cr-Al, Ni_3Al, Fe_3Al, as well as stainless steels, have been studied. The oxide films were deposited by an electrochemical method. It has been shown that the selective oxidation of chromium in Ni-Cr alloys is promoted by surface applied Y_2O_3 and Al_2O_3-Y_2O_3 films. An integral chromia scale was even established on Ni-10Cr alloy. It has also been shown that Y_2O_3 films remarkably decrease the oxidation rate of the Cr_2O_3-forming alloys and the spallation of the scales, but they do not decrease the oxidation rate of the Al_2O_3-forming alloys, although they do reduce the spallation of Al_2O_3 scales. (This work is partly done in co-operation with Stott, F.H., Prof., in the Corrosion and Protection Centre, UMIST).

4. The Oxidation of Ni_3Al and Fe_3Al Intermetallic Compounds

The oxidation kinetics of Ni_3Al and the structure of oxide scales formed on Ni_3Al were investigated. It is shown that the oxidation kinetics of Ni_3Al in pure oxygen at 600-1000°C followed none of the accepted rate laws in most conditions, except the parabolic law under certain conditions. The ordered structure of the alloy had special influences on the nucleation of oxides and the diffusion of reactants in alloy; as a result, oxides with different composition and structure formed on Ni_3Al surface from grain to grain. The oxidation mechanism of Fe_3Al was studied in air at 800-1200°C. It is shown that the oxidation behaviors were quite different in isothermal and cyclic situations. A transgranular internal oxide formed in former condition and an intergranular internal oxide formed in latter condition. A pesting phenomenon was observed after cyclic oxidation. High energy density pulsed plasma (HEDPP) was applied to modify the surface of Ni_3Al and Fe_3Al intermetallic compounds. A microcrystalline layer with grain sizes between 10-100 nm was obtained. The experimental results of oxidation at

1000R: in air showed that a microcrystalline Al_2O_3 scale formed during oxidation, the plasticity and adhesion of oxide scale was remarkably improved, and the oxidation rate decreased and obeyed a fourth power law. An equation for this fourth power law was derived by taking account of the growth of oxide grain size with time and the diffusion along grain boundaries in oxide scales (co-operated with Institute of Physics, Academia Sinica).

5. The Sulfidation of FeMo and FeMoAl Alloys

The sulfidation of FeMo (Mo=20-57wt.%) and FeMoAl (Mo=30, 60; Al=5-20wt.%) alloys was studied in sulfur vapor. The reaction mechanism, evolution of sulfide scale and transportation of reactants through each layer of the scale were studied in details. The sulfidation rate of FeMo alloys decreased exponentially with the increase of Mo amount in alloys. It is proved that, only when a protective Al_2O_3 scale formed on FeMoAl alloy, could these alloys show excellent sulfidation resistance. The formation of Al_2O_3 scale was produced by the selective oxidation of Al in FeMoAl alloys reacted with the residual oxygen in sulfur vapor under normal conditions. In the case of pure sulfur vapor, however, FeMoAl alloys sulfidized at higher rates, which was similar to the sulfidation rate of FeMo alloys containing the same amount of Mo.

6. High Temperature Corrosion of Fe_3Al in Ar+1%SO_2

Catastrophic corrosion of Fe_3Al was observed in Ar+1%SO_2 mixed gas at temperatures above 1000°C. High energy density pulsed plasma (HEDPP) was applied to get a microcrystalline structure scale on the surface of Fe_3Al. It was shown that Fe_3Al after the HEDPP surface treatment showed an excellent corrosion resistance in Ar+1%SO_2 mixed gas at temperatures above 1000°C. Its corrosion kinetics was quite similar to that during oxidation in air at same temperatures, which obeyed a fourth power law. This tremendous result can be attributed to the formation of a compact Al_2O_3 scale promoted by the surface microcrystalization.

7. Fe(Mo,W)Al Coatings

Based on the rather good sulfidation and oxidation resistance of Fe(Mo,W)Al alloys, a technique to obtain the surface coatings of basically the same composition, as well as the content of refractory metals, as high as it could be was investigated. The Fe(Mo,W)Al coatings, with the content of Mo or W higher than about 50wt%, were obtained by Fe(Mo,W) electroplating and subsequent aluminium packing. The coatings are composed of two layers. The outer layer is predominantly FeAl phase. Underneath is an enriched W layer. The corrosion results under the environment with 10^{-21}Pa oxygen pressure and 103Pa sulfur pressure at 800°C demonstrated that both of those two sorts of coatings were corroded severely. If the oxygen pressure in the environment is increased to 10^{-3}-1Pa and the sulfur pressure kept unchanged, however, the corrosion rates decreased remarkably. So a trivial amount of oxygen in the environment can greatly improve the corrosion resistance by promoting the establishment of Al_2O_3 scales on the surface of the coatings. Their corrosion rates are comparable to the growth rate of Al_2O_3 scales. In order to promote the corrosion behaviour of the coatings, to change from sulfidation to oxidation in the environment, with high sulfur pressure and low oxygen pressure, a mixed Fe_2O_3-SiO_2 scale was applied to the top of the coatings. In this case, a selective Al_2O_3 scale formed underneath the Fe_2O_3-SiO_2 scale which provides the coatings and the substrate of alloys with a good resistance to sulfidation in the environment of high sulfur pressure.

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SCOPE OF RESEARCH

Fundamental Approach

The thrust of the research is the role of high-temperature oxide scales in the protection of metals, alloys and coatings, with emphasis on their mechanisms of growth, protective properties and breakdown in aggressive situations, such as low oxygen, high sulfur or chlorine, potential, wet oxygen and molten salts environments. The research includes fundamental studies of the development of protective scales and the effects of reactive elements, growth stress, and in some corrosive situations where protective scales are not stable. Examples include coal conversion, or gasification, or waste-fired boiler environment, gas turbine environments where molten salts may be deposited and fluidized-bed coal combustion conditions where impact erosion by solid particles may cause degradation. The alloy-oxide interface has been examined by TEM and HRTEM. The processes of the development of protective oxide scale on the sputter deposited, microcrystalline MCrAlY coating have been studied.

Applications, Engineering Achievements and Technology Transfer

The sputter coated MCrAlY coating on turbine blades made by NiAl intermetallics and modification of aluminized coating by dispersion of rare earth oxide particles, and their effectiveness for protection of turbine blade, have been studied. Extensive programs are also examining the role of anti-permeation of hydrogen (tritium) by the development of alumina scale on 316L stainless steel. Application of the aluminized coating has been extended to protect some thermal parts in petroleum refining and petrochemical industries.

Specific Topics

1. High Temperature Corrosion of Alloys

1.1 TEM and HRTEM Studies of Oxide Scale

A Ni-La_2O_3 composite film has been developed by the technique of co-electrodepostion of La_2O_3 dispersed particles with nickel onto a pure nickel plate surface. High resolution electron microscope (HREM) revealed that in the codeposited film a number of La_2O_3 nanocrystals with diameter below 5 nm appeared as dispersions. The isothermal oxidation kinetics in air at 900 °C and 1000 °C showed that the Ni-La_2O_3 film-coated nickel plate resulted in a significant reduction in oxidation rate in comparison with that of the plates without and with pure nickel film deposited. In addition, specimens of Ni-La_2O_3 film-coated nickel plate also exhibited excellent resistance to cyclic oxidation in air at 1000 °C; conversely, the other two La_2O_3-free specimens deformed considerably at their corners and edges and the scales grown on them cracked severely. Moreover, the NiO scale formed on the composite coating showed an average grain size that was a factor 6~15 smaller than that of the scale formed on nickel plate, with and without a nickel coating. Electron probe microanalysis (EPMA) results showed that La_2O_3 dispersed in the outer part of the NiO scale, with a thickness corresponding to that of the original codeposited film. Transmission electron microscopy observed that La_2O_3 particles, in the diameter range from 20 to 500 nm, were incorporated in the NiO grains as well as along their grain boundaries. It is proposed that the modification in oxidation behavior of nickel plate by the codeposion of Ni-La_2O_3 may be attributed mainly to the formation of La_2O_3-modified NiO as an outer part of the scale, in which rapid outward-diffusion of nickel along short-circuit paths may be inhibited due to the segregation of La ions into the grain boundaries of the NiO, and also due to possible, partial dissolution of small La_2O_3 nanoparticles originally present in the codeposited film.

1.2 Defect Detection in Al_2O_3 Oxide Scale by SPA Technique

This is conducted on Al_2O_3-forming alloys, such as FeCrAl and NiAl. The amount and distribution of the defects in Al_2O_3 scale grown on the RE doped and un-doped alloys are measured by the Slow Positive Electron Annihilation technique. Both the electrical conductivity and microstructure of the scales, doped and un-doped, are measured by electrochemical current-impedance technique and TEM. A mechanism based on the theory of permeation flux is suggested for reactive element effects.

1.3 High Temperature Corrosion of Superalloys

High temperature oxidation behavior of Ni-based superalloys M17, K3 and highly homogenized superalloy M41 has been investigated. Experiments including isothermal and cyclic oxidation, XRD, SEM, EDAX have been performed. Results show that the oxidation rate of alloy M41 increases with temperature, but is lower than that of alloy K3. Scale adherence of alloy M41 is better than that of alloy K3 and M17; its cyclic oxidation performance is superior to that of alloy M17. Oxidation kinetics of alloy M41 obviously deviate from the parabolic law because of the volatilization of CrO_3 above 1000°C. The higher the temperature is, the greater the deviation. In the steady oxidation stage, the scale consists mainly of a continuous and compact Cr_2O_3 oxide outer layer and a tree-root-shaped Al_2O_3 internal oxide zone. The internal oxidation becomes more severe with the rise of temperature and exposure time. The simultaneous addition of 0. 1%S, 0. 005%P and 0. 1%Zr in the alloy M17 increased its oxidation rate, and addition of 0. 1%Zr improved the adherence of the scale.

Hot corrosion behavior of alloys K3, M38G and M41, with 0.5mg/cm^2 Na_2SO_4 coating, at 900°C has been investigated. Both alloys M41 and K3 are subjected to catastrophic hot corrosion in a short time. The weight loss of alloy M41 is rather less than that that of K3, but the corrosion products of M41 penetrate into its substrate more severely than those of K3 do. Alloy M38G has a good resistance to hot corrosion of pure Na_2SO_4 at 950°C. The acidic fluxing can explain the hot corrosion behavior of alloy M41. The accelerated hot corrosion of alloy M41 can be inhibited by pack aluminide coating. The electrochemical impedance technique for the evaluation of hot corrosion behavior of superalloys, coatings and intermetallics in molten salts has been developed, in order to illustrate the electrochemical aspect of hot corrosion especially to understand the corrosion process concerning a fuel cell.

1.4 High Temperature Oxidation of Fe-Cr Alloys in Wet Oxygen

Fe-Cr binary alloys have been oxidized in a stream of oxygen containing different amounts of water vapor at 900-1000°C to study the effects of water vapor. The Fe-Cr alloys exhibited an initial protective behavior due to formation of Cr-rich scale and was succeeded by a non-protective, breakaway oxidation due to formation of iron-rich scale. The appearance of the breakaway oxidation was very sensitive to the water vapor content in the atmosphere. The higher the water vapor content, the earlier the taking place of the breakaway oxidation. Increasing the oxidizing temperature or decreasing the Cr content in the alloys facilitated the earlier breakaway oxidation. The breakaway oxidation was inhibited effectively by surface applied CeO_2 particles before oxidation. A mechanism of the effects of water vapor based on the observed results and analysis of local reducing condition caused by H_2O molecule has been proposed.

1.5 High Temperature Corrosion of Rare-Earth-Element-Containing Alloys in Gas Mixtures

A project supported by European Community under fixed contract No. CI1*-CT94-0007 has been conducted since 1995 jointly with collaboration of the team of Gesmundo, F., Prof., of the University of Genova of Italy, aimed at illustrating of the corrosion behavior of rare earth metals such as yttrium and cerium containing iron-and cobalt-based alloys in purely oxidizing, and sulfidizing gases as well as in mixed sulfidizing-oxidizing mixtures of the coal gasification type, i. e. with high sulfur and low oxygen pressures. The main objectives of the study are firstly because the corrosion behavior of these alloys has never been studied; thus the results are of significant interest from the point of view of the fundamental research and secondly this study would be expected to allow identification of new materials, or coatings, which would be candidates for the relevant industrial environments.

1.6 High Temperature Chloridation of Ni-20Cr Alloy

The high temperature chloridation behaviors of Ni-20Cr alloy in a $(HCl+H_2)$ gas mixture have been studied. Thermodynamic calculation predicted that there are two different regimes of stable chloridation products, depending on the gas ratio of P_{HCl}/P_{H2} and the temperature. In the regime of lower ratio of P_{HCl}/P_{H2} and higher temperature, the only important chloridation product is volatile $CrCl_2$(g), and in the regime of the higher ratio of P_{HCl}/P_{H2} and lower temperature, the condensed phase $CrCl_2$(c) becomes thermodynamically stable. The chloridation kinetics' study was carried out in the two different regimes by TGA measurements. A time-dependent mass loss rate was observed in the first experimental regime. Further analysis of the kinetic data indicated that the chloridation rate limiting process is a combination of a linear gas phase transport in series with a parabolic process of the substrate diffusion of Cr. In the second experimental regime, the growth of condensed product leads to mass gain behavior. The surface of the alloy after chloridation in the first regime showed pitting morphology. A surface scale was visible for the alloy after chloridation in the second regime. These observations are consistent with the expectations of the thermodynamic analysis and the results of kinetic measurements.

1.7 Internal Oxidation of Ag-Cu Alloy

The internal oxidation (at 750°C and 850°C) of Ag-Cu, alloys with the Cu atomic percentage respectively 0.8, 3.3, 6.3 and 9.5, has been studied. It was found that CuO particles precipitated homogeneously on the surface of Ag-Cu alloys except for Ag-9. 5at%Cu, on the surface of which was exhibited the agglomerated precipitation of CuO particle clusters. The experimental results also revealed that the nucleation and growth of CuO oxide evenly varied with the change of Cu contents or oxidation temperature, when both Cu content and exposure temperature were lower. The precipitation, as well as the growth of internal CuO oxide, were consistent with the prediction by the classical Böhm-Kahlweit mode, but the abnormal phenomenon of nucleation and growth of the CuO oxide was observed when the Cu content or the exposure temperature was increased. As a result of investigating the atomic structure of different internally oxidized Ag-Cu alloys, it is proposed that stacking fault tetrahedral (SFT), which was found in the oxidized alloys, promoted the nucleation of CuO internal oxide.

1.8 High Temperature Corrosion of Intermetallics

High temperature oxidation and hot corrosion of Ni-Al and Ti-Al intermetallic alloys in a variety of corrosive environments were evaluated. Ni-Al intermetallics were susceptible to cyclic oxidation and hot corrosion, although they exhibited resistance to isothermal oxidation to some extent. Hf and B were beneficial to the oxidation behaviors of the alloys, whereas Fe and Mo have detrimental effects on the oxidation and hot corrosion resistance. Ti-Al intermetallics showed poor oxidation resistance above 700°C. The effects of several coating systems upon the corrosion behaviors of the alloys were investigated. NiCrAlY coatings showed no harmful effects on the mechanical properties of Ni_3Al-based alloy IC-6. Moreover, the thermal fatigue property of guide vanes made of alloy IC-6 was improved by sputtered NiCrAlY. Due to the inward diffusion of Co and Ni into the substrate for MCrAlY/TiAl system, however, two brittle and hard diffusion layers formed at the coating/substrate interface. Such severe interdiffusion would influence the long-term oxidation resistance and the mechanical properties of alloy. Sputtered TiAl coating with Cr addition on Ti-Al remarkably improved the oxidation resistance of Ti-Al alloys due to the formation of a protective Al_2O_3 scale. Little interdiffusion occurred at the coating /substrate interface. This coating may be a practical coating for Ti-Al alloy. Reactively-sputtered Al_2O_3 film was very effective to improve the oxidation resistance of TiAl alloy below 900°C. However, the thermal expansion mismatch resulted in the poor cyclic oxidation resistance.

2. Mechanical Behavior of Oxide Scale

2.1 Measurement of the Stress in the Oxide Scale

A new method for stress measurement of the oxide scale by cantilever bending with a strip sample oxidized on its two sides has been developed. The influence of yttrium implantation on the growth stress of Al_2O_3 formed on Co30Cr6Al sputtering coating and β-NiAl diffusion coating was investigated. The change of the growth stress due to the RE implantation can be measured precisely by using the new method. The residual stress of oxide scale formed on Co40Cr alloy, with and without yttrium implantation, Ferroalloy and MA956 was measured by using Raman spectroscopy. The studies mainly concerns the stress distribution in the scales and the stress amplitude in the local area where the oxide grain boundary or physical defect may exist.

2.2 Mechanism for Cracking and Spalling of Oxide Scale

The objective of the research is to understand the cracking process of the protective oxide scales of Al_2O_3 and Cr_2O_3. The main technique used is acoustic emission/AE spectrum analysis. Because of the remarkable effect of the pre-existing physical defects at the oxide/ metal interface on the adherence of the oxide scale, the amount and distribution of the pre-existing physical defects have been measured using an AE technique, particularly for the RE effects. The Cr_2O_3 formers of yttrium-implanted Co40Cr and Ni30Cr are selected for this study.

2.3 Evaluation of the Adherence of Oxide Scale

The purpose of the research is to evaluate the fracture strength and the adherence of the oxide scale by four point bend/AE and pull-off tests. The mechanical failure of the oxide scales formed on Fe23Cr5Al and Fe23Cr5Al(Si, Ti, Y) oxidized at elevated temperature(1000-1200°C) is studied at ambient temperature. This work is also extended to some protective coatings.

3. Erosion-Oxidation of High Temperature Alloys

A test facility for the combined effect of high temperature erosion-oxidation in gas-solid stream has been set up. The test samples mounted on a rotating holder move relatively to a stream of high-temperature fluidized solid particles to generate the erosion-oxidation effect. The maximum temperature of the facility is 900°C; the maximum velocity relative to the two phase stream is 15m/s. The erosion oxidation behavior of 310 stainless steel and HK40 alloy have been tested at 700°C. Both alloys exhibited erosion enhanced oxidation behavior under test conditions.

4. Protective Coatings

4.1 Modified Aluminide Coating with RE Oxide Dispersion

Based on the observations of the effects of RE oxide dispersed on the improvement of oxidation resistance of the aluminide coating, the processes and effectiveness of the modified aluminide coating with RE oxides dispersion on turbine blades are investigated. Both aluminide and silicon-aluminide coatings with CeO_2 dispersed are produced on either conventional cast Ni-base alloy or directionally-solidified alloy. Their corrosion resistance is tested at temperature up to 1100°C. The apparatus for the coating deposition and optimizing process has been developed.

4.2 Thermal Barrier Coatings

The aim of the work is to simulate the thermal stress distribution in thermal barrier coatings on turbine blades by the finite element method. Both the loading status and blade shape are considered in the process of computer simulation. Higher loading level and loading rate produced larger thermal stress values, and the back side of the blade has the largest stress value, while the exhausted edge has the lowest. The stress concentration zone in the vicinity of the bond layer/ceramic layer interface is analyzed in detail. Some modifications to increase the lifetime and reliability of TBCs are suggested.

4.3 MCrAlY Overlay Coatings

The work is an investigation of the formation and degradation of the sputtered overlay coatings, with emphasis on the microstructure of the coatings and the performance of the coatings on superalloys, intermetallic compounds of Ni_3Al and TiAl at high temperatures and in a hot-corrosion environment. The influence of Ta and TaN barriers on diffusion of aluminum in the coating and oxidation kinetics of the coating are studied. An investigation is being undertaken of the effects of reactive elements such as yttrium and the microcrystallization of the overlay coating on the oxidation and/or hot-corrosion resistance.

4.4 Microcrystalline Superalloy Coatings

An investigation is being undertaken into the microstructure of the sputtered microcrystalline superalloy films and their performance at high temperatures. The emphasis of the investigation is laid on the effects of microcrystallization on the oxidation of the superalloy. The mechanisms may be the change of oxide scales from complex oxides of Cr_2O_3, TiO_2 and Al_2O_3 to unitary oxide Al_2O_3 on microcrystalline superalloy coatings and/or the improvement of the adhesion of the oxide scales on the surface. The formation and the rehealing ability of the protective oxide scales and the excellent adhesion of the oxide scales to the microcrystalline superalloy coatings are being investigated.

4.5 Selective Solar Films for High Temperature Application

The investigation of selective solar films for application above 600°C is been undertaking. The films were produced by dc reactive sputtering from a metallic alloy target. A comprehensive kinetics modal for dc reactive sputtering was proposed to interpret the dependencies of reactive gas flux thresholds upon the history of gas flux. Nanostructure, percolation, optical properties and oxidation behaviors of the oxide-alloy composite films were studied.

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SCOPE OF RESEARCH

1. High temperature corrosion in mixed gaseous environments.
2. Effects of alloying elements on high temperature corrosion resistance etc.

CZECH REPUBLIC

CONTENTS

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SCOPE OF RESEARCH

Specific Topics

1. *Precipitation Processes and Mechanical Properties of Duplex Stainless Steels at Elevated Temperatures*

The research deals with the relationships between precipitation reactions and basic mechanical properties in two grades of duplex stainless steels after isothermal annealing at the temperatures 450, 550 and 590°C. The precipitation of minor phases was observed only at γ/δ interfaces and inside ferritic grains. Precipitation reactions were dependent on the chemical compositions of steel, particularly the contents of Si, Cr, Mo and N. Due to precipitation processes during isothermal annealing at 450 and 550°C, especially spinodal decomposition of ferrite, the strength parameters of both steels were increased. Different mechanisms of ferrite decomposition during annealing at 590°C resulted in a decline of strength due to premature failures.

2. *Nitriding and Hydrogen Attack on 2.25 Cr-1Mo Steel in Ammonia Systems Gas Converter*

Certain ammonia synthesis conditions lead to nitriding of a relatively thin surface layer of low-alloyed 'hydrogen-resistant' steels. For reasons of the thermodynamic stability of carbides and nitrides this causes a modification of the first, releasing carbon which can effuse from the steel and can react with diffusing hydrogen to form methane. Depending on the level and the direction of the total component stresses, small separations of grains, parallel to the surface, or cracks across the wall may slowly develop. Thus nitriding by ammonia synthesis gas causes a modification of the carbides, a decarburization and sensitization to hydrogen attack within a relatively thin metal layer near to the inner surface of the converters. Subsequently, a sensitization to hydrogen attack occurs due to the reaction of diffusing hydrogen with carbon released by the carbides and a decarburization by carbon diffusion to the surface. High local internal stresses perpendicular to the surface, caused by surface nitriding, lead to small intergranular separations parallel to the surface without any significant effect on the integrity of the pressure vessel. As the nitrided layer hinders further nitriding of the steel, this phenomena is without any long-term consequence.

On the other hand, if a sufficiently high load and/or residual stresses apply in the axial or tangential direction to the vessel wall, cracks have to be expected propagating slowly across the wall, as crack growth is controlled by diffusion of nitrogen and carbide transformation. Consequently, the Nelson diagram for NH_3-containing synthesis gas should be applied only with great care. Efforts are necessary to quantify as well the critical stress level for crack initiation, as the propagation rate of such cracks is controlled by nitrogen diffusion and the complex carbide reactions finish by classical chemically induced hydrogen cracking.

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Scientific Key Words: Oxidation; Sulfidation; High temperature corrosion; Ion implantation

Technical Key Words: Coal gasification; Waste incineration

SCOPE OF RESEARCH

The problems of high temperature corrosion in gases has been studied in SVUM for many years (since 1952 - Vyklický, M., Cizner, J.). Recently the laboratory participates in the European programs (COST 501 and 515) and programs of the National Grant Agency. Laboratory is equipped by 6 furnaces (up to 1250°C) and tests can be performed in various aggressive atmospheres. Corrosion tests are evaluated in up-to-date gravimetric, metallographic and other physical and chemical methods.

Specific Topics

1. *Laboratory Evaluation of Corrosion of Metal Materials (and Protective Coatings) is Undertaken, Including Kinetics and Mechanisms*

   a) in a coal gasification environment;

   b) in a waste incineration environment;

   c) in pyrolysis gases in chemical industry.

2. *Long Time (up to 5000 hours) High Temperature Corrosion Tests in a Broad Spectrum of Gaseous Environments are Performed:*

   a) under laboratory conditions;

b) as field tests.

3. Service Life Estimation of Plant Parts on the Basis of an Extrapolation of the Long-Term Corrosion Tests Results is in Progress.

4. Evaluation of the Influence of IBAD (Ion Beam Assisted Deposition) SiN_x Coatings on the High Temperature Corrosion Resistance of Steels is Being Investigated.

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2. Pitter, J., Cizner, J. and Bína,V., "Corrosion Behaviour of the Austenitic Steel in Sulphidizing Environment," Proceedings of the 9th Symposium on Metallography, Tatranská Lomnica - Stará Lesná, Slovakia, 529-531 (1995).

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5. Cizner, J., Pitter, J. and Hakl, J., "Contribution to the Laboratory Testing Methodology of the High Temperature Corrosion in Gaseous Mixtures," Proceedings of the Conference EUROCORR 96, Ses.III, P 7, Nice (1996).

6. Cizner, J., Pitter, J., Hakl, J. and Leitner, J., "Influence of Coal Gas Environment on Some Metallic Materials Behaviour at High Temperature and Long Exposure," Proceedings of the Conference EUROCORR 96, Ses.III, OR 22, Nice (1996).

7. Pitter, J., Cizner, J., Èerný, F., Djouadi, M.A. and Koutsomichalis, A., "The Influence of Gradient SiN_x IBAD Coatings on Corrosion Resistance of the Alloyed Steels in Sulphidizing - Oxidizing Atmosphere at High Temperature," Proceedings of the 5th International Conference on Plasma Surface Engineering, Garmisch - Partenkirchen, Germany (1996).

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Conference on the Effect of Non-Standard External Factors on Physikal Properties of Solids, Kocovce, Slovakia, p73 (1996).

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Scientific Key Words: High temperature water corrosion; Monitoring

Technical Key Words: Nuclear reactor; Cladding/coolant reaction; IASCC; SCC; Radiation build-up

SCOPE OF RESEARCH

High Temperature Corrosion in Nuclear Reactor Systems

The thrust of the work is experimental research in the field of environmental degradation of material used in primary and secondary circuits. It includes high-temperature water with additives, radiation and mechanical stresses of specimens. The research also involves corrosion products' release, activation and deposition. The experimental base is formed by a high-pressure in-pile loop (PWR and BWR conditions) and other out-of-pile facilities. Extensive programs have also examined the role of different water chemistries like standard, high pH, hydrazine in the mass activity transfer. Relevant developments include preconditioning of the metal surface by the formation of protective layers which minimise corrosion product release. The experimental base also enables special services for nuclear plants or industry vendors: steam generator tubes testing involving crack propagation, tube plugs etc. Testing of different materials includes SCC, IASCC and corrosion fatigue by CT (1CT, 2CT) or SSRT types of specimens.

Here, reference is restricted to aspects relevant to high-temperature corrosion in the context of this survey.

Specific Topics

1. Environmental Degradation of Materials

A special system of an irradiation channel, equipped with loading systems enabling 1CT, 2CT or SSRT samples, is used. The channels are connected both to a pressurized and a boiling water loop, so both water chemistries are achieved during irradiation. For the boiling water loop, ECP measurement is used to establish the oxidising environment. The 2CT channel enables cyclic stress of 151 kN and neutron irradiation, the two channels are utilized, one with radiation and the second without radiation, in the same run. The main reason is to understand the influence of neutron and gamma dose rate on corrosion phenomena.

2. Cladding-Coolant Interaction

Corrosion of zirconium alloys for fuel cladding is studied. The experimental research investigation involves the cladding temperature, water chemistry, the heat flux and radiation. Testing facilities consist of electrically heated rods with a power flux of 100 W/cm. Emphasis is being placed on the influence of water chemistry, including lithium, potassium, ammonia, hydrazine and boric acid; increased lithium over pH>7.4 and to surface nucleate boiling and synergistic effects of radiation. Eddy current measurement is used for corrosion layer determination.

3. Corrosion Product Release, Deposition and Activity Transport

One purpose rigs are used to study corrosion product release, deposition and activity transport. The rig (Micro loop) models thermohydraulic, material and water chemistry conditions of primary circuit of PWR, VVER or BWR reactors. A post-irradiation study is performed by using different techniques: radioactivity deposition, corrosion product layers, morphology, and phase composition on the surface. The techniques include gamma spectrometry, TEM, SEM and EDAX and in special cases X-ray diffractometry, Mössbauer or infrared spectroscopy. For water analysis, Orbisphere O_2H_2) analysis, high temperature conductivity and ion-chromatography are used. The computer code DISER was developed for the modeling of corrosion product radionuclides behavior in primary systems.

RECENT PUBLICATIONS

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5. Kysela, J., Všolák, R. and Erben, O., "Research Facilities of LVR-15 Research Reactor, ENS," Topical Meeting on Research Facilities for the Future of Nuclear Energy, Brussels, May (1996).

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Scientific Key Words: Ash; Chlorine; Hot corrosion; In-plant monitoring; Lifetime; Molten salts; Steam oxidation

Technical Key Words: Advanced steam conditions; Biomass combustion; Circulating fluidized-bed combustor; Steam boiler; Ultra-supercritical plant; Straw-fired boilers

SCOPE OF RESEARCH

Fundamental Approach

ELSAM is an electric utility consortium of independent power companies in the western part of Denmark. ELSAM intends to reduce CO_2 emissions by building and operating high-efficiency coal-fired boilers and biomass-fired plants. Higher steam temperatures up to 580°C and the combustion of corrosive biomass fuels, typically straw, have forced ELSAM to initiate research and development into steam oxidation and high temperature corrosion. The R&D work is concentrated on full-scale tests at various boilers (PF, CFB and vibrating-grate) fired with coal, coal/straw mixtures and in some cases straw alone; also waste incineration has been a subject for research. Steam oxidation in evaporators and superheaters of ultra-supercritical boiler is studied with the aim of limiting material temperatures in order to extend lifetime due to corrosion and creep. Computer-based lifetime models have been made for calculation of superheater and evaporator lifetime incorporating literature and plant oxidation data. High temperature corrosion in straw combustion and coal/straw co-combustion are other research areas which have been studied in full-scale tests with a normal duration in the range of 1000-2000 hours. During the test, temperature-regulated corrosion probes are inserted, deposits are sampled, ash is sampled, boiler service parameters are monitored and combustion may be video-monitored for short periods. Corrosion losses are determined by precision measuring with a combination of a pre-exposure measurement of the wall thickness with a micrometer screw gauge and a post-exposure measurement of the remaining and unaffected wall thickness in a light optical microscope, or with a profile projector. Test pieces, including ash deposits, were investigated by means of scanning electron microscopy with energy dispersive analysis by X-ray (SEM/EDX) in order to acquire more detailed information for evaluation of corrosion mechanisms.

Applications, Engineering Achievements and Technology Transfer

The research of Faelleskemikernes Materials Group is closely related to the technology in focus in the ELSAM utility consortium. The relevant technologies include ultra-supercritical pulverized coal-fired units, coal/straw fired CFB boilers, coal/straw co-combustion on pulverized coal-fired units and straw combustion in grate boilers.

1. Steam Oxidation in Evaporators and Superheaters

The research is carried out by ELSAM, to a small extent in co-operation with the Danish boiler manufacturer Burmeister & Wain Energy. Steam oxidation data of boiler materials are extracted from the literature, oxide deposition rates, as well as oxide porosities of evaporator tubes, are investigated on samples from evaporator tubes of supercritical boilers. Computer-based lifetime models are made for superheater and evaporator tubes. The models are used in design considerations and remnant lifetime analysis.

2. High Temperature Corrosion in Biomass-Fired Boilers

Full-scale tests have been carried out on two PF boilers co-combusting coal and 10-20% straw, a CFB boiler co-combusting 50% coal and 50% straw, and a 100% straw-fired vibrating grate fired boiler. The work has been carried out in close collaboration with in the Combustion Group under the Department of Chemical Engineering and Corrosion and Surface Technology, Institute of Manufacturing Engineering both at the Technical University of Denmark. A good understanding of the corrosion mechanism related to straw-firing has been achieved enabling the modification of combustion and boiler design in order to prevent high corrosion rates.

RECENT PUBLICATIONS

1. Steam Oxidation

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2. Henriksen, N., Larsen, O.H. and Blum, R., "Lifetime Evaluation of Superheater Tubes Exposed to Steam Oxidation, High Temperature Corrosion and Creep," Power Plant Chemical Technology Conference, Kolding, 4-6 September (1996).

2. High Temperature Corrosion by Straw Combustion

3. Henriksen, N., Larsen, O.H., Blum, R. and Inselmann, S., "Requirements for the Co-Combustion of Coal and Straw," The Institute of Materials Conference "Materials Issues in Heat Exchangers and Boilers", Loughborough, October (1995).

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5. Larsen, O.H. and Henriksen, N., "Ash Deposition and High Temperature Corrosion at Combustion of Aggressive Fuels," Power Plant Chemical Technology Conference, Kolding, 4-6 September (1996).

6. Henriksen, N. and Larsen, O.H., "Fouling and Corrosion in Straw and Coal-Straw-Fired USC Plants," 9th European Bioenergy Conference, Copenhagen, June (1996).

7. Hansen, P.F.B., Lin, W., Johansen, K.D. and Henriksen, N., "Can Superheater Corrosion During Co-combustion of Straw and Coal in a CFB-Boiler be Reduced?," 5th International Conference on Circulating Fluidized Beds, Beijing, May (1996).

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Scientific Key Words: Adhesion; Chromia; Coating/modifying surfaces; ODS alloys

Technical Key Words: Fuel cells; Solid oxide fuel cells

SCOPE OF RESEARCH

Specific Topics

1. High-Temperature Oxidation Studies of ODS Cr-Rich Alloy

For the interconnection of the cells in a solid oxide fuel cell stack a metallic ODS Cr-rich alloy is being investigated. The Cr5Fe1Y_2O_3 alloy is fabricated at Metallwerk Plansee, Austria. The microstructure, especially the distribution and size of the yttria, has been studied. The oxidation behaviour in various atmospheres (dry and wet air, dry and wet H_2/Ar, simulated reformed natural gas) has been studied. The oxidation temperatures have been in the range 850°C to 1600°C. Several of the oxidation studies were performed by thermogravimetry, followed by evaluations by XRD and SEM. For use in a solid oxide fuel cell, the adhesion of the oxide scale to the metal must be good in order to obtain a low electrical resistance through the metal and scale. The thickness of the chromia scale must then also not extend more than a few µm. Attempts at improvement of the electrical contact between in the alloy and the solid oxide fuel cell is being carried out. One attempt has been coating the alloy with ultrafine particles of La- and Sr-oxide. During heat treatment the chromia formed as a scale may be expected to react with the coating to form a coating of $La_{1-x}Sr_xCrO_3$ (LSC). This oxide is highly conducting at operating temperatures. The formation of the LSC coating has been confirmed. The work has in part carried out in collaboration with Haldor Topsø A/S, Denmark.

2. Fundamental High-Temperature Oxidation Studies of Fe-Cr Alloys

Fe-Cr alloys with Cr-contents of 0, 20, 30, 40, 50, 60 and 100 wt% have been studied. The technological interest is whether the Fe-rich alloys are applicable for the use as a metallic interconnect material in solid oxide fuel cells (SOFC). For use in a SOFC stack the difference, in thermal expansion, between the alloy and the ceramic components of the cell, should not be too great. The thermal expansion has therefore been measured, in dry H_2/Ar, for the alloys between room temperature and 1100°C. The oxidation behavior of the alloys in wet air and wet H_2/Ar has been investigated by thermogravimetry at temperatures up to 1300°C. Selected alloys have been coated with ceria by immersion in an aquous Ce-nitride solution. The coating is found to improve the oxidation behaviour significantly. After the oxidation the samples are investigated by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Selected samples have been investigated by transmission electron microscopy (TEM). In-situ SEM studies of the oxidation of Fe30Cr in saturated water vapour was performed at 1000°C by the use of an environmental SEM (ESEM). Long-term oxidation studies of coated and uncoated Fe-Cr alloys have also been carried out at 1000°C in an atmosphere of simulated reformed natural gas. The work has in part been carried out in collaboration with Haldor Topsøe A/S, Denmark and Oslo University, Norway.

RECENT PUBLICATIONS

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Scientific Key Words:	Mixed gases; Salt deposits; Modeling gas-metal reactions
Technical Key Words:	Advanced steam conditions; Biomass combustion; Waste-fired boiler; Straw-fired boilers

SCOPE OF RESEARCH

Fundamental Approach

The main aim of the research is to achieve a greater understanding of the corrosion processes in aggressive environments associated with power production, primarily with respect to superheater corrosion, and thereby support the developments within the power production industries in Denmark with regard to the utilisation of biomass as a fuel type.

Applications, Engineering Achievements and Technology Transfer

In this work, there is contact with the power companies in Denmark in the assessment and characterisation of future materials to function at higher steam temperatures and pressures and in biomass fuels, namely straw-fired and waste-fired power plants.

1. *High Temperature Corrosion of Superheater Materials for Power Production through Biomass*

This research is based on corrosion of superheaters in straw-fired boilers and waste incinerators. The project is being carried out in collaboration with Materials Department RISØ and The FORCE Institute. The research consists of laboratory studies where an AISI 321 type steel and Sanicro 28 are exposed to a synthetic flue gas environment containing SO_2 and HCl in the quantities typically found in straw-fired power stations. In addition, specimens are exposed to the ash deposits typically found on superheaters in straw-fired power plants (containing primarily KCl and K_2SO_4), or are exposed to both ash and aggressive flue gas environments. Thus, the relative contributions of flue gas and ash corrosion can be revealed. In addition, thermodynamical modeling is undertaken to support the experimental observations. Another part of the projection is the collection and characterisation, using SEM and XRD, of ash deposits from over 20 biomass fired power plants in Denmark. This work is supported by the Danish Ministry of Energy.

RECENT PUBLICATIONS

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4. Montgomery, M., and Maahn, E., "Laboratory Study of High Temperature Corrosion in Straw-fired Power Plants." Proc. Eurocorr '97, Trondheim, Norway. Vol. II, 41-46 (1997).

FINLAND

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Scientific Key Words: Reducing environments; Sulfidation; Melts; Hot corrosion; Thermodynamic modeling; Coatings; Intermetallics

Technical Key Words: Pulp/paper boiler; Circulating fluidized-bed combustor; Biomass combustion; Boiler tube failures; Industrial furnaces

SCOPE OF RESEARCH

Fundamental Approach

In the research and collaborative efforts in the Institute, the understanding of process and corrosion chemistry in a joint manner is emphasized. Corrosion of metals and alloys in various complex mixtures of alkali metals and chalcogens, forming various solid or liquid alloy phases, are considered. Recent theoretical and experimental work has concerned the stability of Fe-Cr-Ni alloys in low-melting mixtures of sodium and potassium sulfides and chlorides in process conditions, where sulfur and alkali metal potentials are high, and oxygen potential is low. This work was done in collaboration with Backman, Rainer, Dr., at Åbo Akademi University, Turku, Finland, where theoretical and experimental studies of low melting mixtures of alkali metal sulfates, carbonates, and chlorides are now in progress. Studies on the stability and properties of various corrosion products of transition metals will be joined to that work. In addition, special attention is paid to surface chemistry and to novel experimental methods. Fundamental physico-chemical aspects of the thermal spraying process and coating-substrate interaction are studied in order to optimize coatings for various high-temperature applications.

Applications, Engineering Achievements and Technology Transfer

The research work in the field of high-temperature corrosion is undertaken to solve corrosion and material-related problems in the industry. The bias of the applications is in the pulp and paper industry where the continuous development of process and environmental technology creates new, and frequently unique, corrosion environments.

1. Corrosion of Steels and Alloys in Black Liquor Recovery Boilers (BLRB)

This work has been done, in part, in collaboration with Åbo Akademi University and Helsinki University of Technology. The aim of the present work is to establish corrosion properties of various chromium- and nickel-containing steels and alloys in BLRBs. The effects of variation and trends in process parameters on the materials choice are assessed. Material developments considering the needs in future are surveyed.

2. Applications of Thermodynamic Data, Phase Diagrams and Modeling in Materials Technology for High-Temperature Processes

This work has been done in collaboration with Helsinki University of Technology and Åbo Akademi University. The essence of the co-operative work is to evaluate and combine basic data on various chemical systems for modeling calculations. Recently, various systems important in the corrosion and degradation of structural materials in the boiler or furnace technology have been considered. Growing attention will be paid on the modeling of the high-temperature water environment. The use of modeling as a dynamic part of knowledge structures in high-temperature corrosion databases is presently developed in collaboration with Hämäläinen, Marko, Dr., at JRC Petten.

3. Prospects of Surface Engineering and Materials Technology

This work has been done in collaboration with Tampere University of Technology and Helsinki University of Technology. The aim is to find out applications of new materials and manufacturing technologies, e.g., in the field of industrial high-temperature processes. Recent interests include characterization of the properties of HVOF-coatings and optimization of the spraying process, and applications of intermetallics including silicides.

RECENT PUBLICATIONS

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3. Salmi, J., "Lining Life of Ceramic Fiber Materials in Fuel-Heated Industrial Furnaces," In: Energy-Efficient Steel and Metal Production on the Energy Research Programme 1988-1992, Eds. Hakulin and Håkan, Helsinki Ministry of Trade and Industry, 1993, pp64-66 (Ministry of Trade and Industry, Energy Department, Review B:169) (1993).

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2. Surface Engineering and Applications of Advanced Materials Technology

8. Mäkipää, M., Hirvonen, J.-P. and Likonen, J., "Erosion of Some HVOF Sprayed Coatings in Fluidized Bed Circumstances," In: Thermal Spray Coatings Research, Design and Applications Proceedings, Eds. C. Berndt and T. Bernecki, Anaheim, Calif., 7-11 June 1993. Ohio: ASM International, 179-184 (1993).

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10. Keskinen, J., Tiainen, T., Lagerbom, J., Korpiola, K., Ruuskanen, P. and Hannula, S-P., "Potential of Metal Aluminides for Industrial Applications," Nordisk Konferens i Pulverteknik 90, Stockholm, Sweden, 21-22 November 1995, p1 (1995).

11. Hannula, S.-P., "Recent Advances in Surface Engineering Applications," In: Advanced Materials and Technologies, Ed. V. Lindroos, Espoo, Helsinki University of Technology, 1995, 351-368 (1995).

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Scientific Key Words:	Diffusion; High temperature fatigue; Carbon-carbon composites
Technical Key Words:	Future gas turbine materials; Blades; Diffusion barrier; Superalloys;

SCOPE OF RESEARCH

Fundamental Approach

The blades of the hottest zone of the gas turbine are often of Ni-base superalloys, protected against high-temperature oxidation by an overlay of MCrAlY or aluminides. At temperatures above 1000°C, Ni from the superalloy tends to diffuse into the overlay, and consequently Al from the overlay into the superalloy. The former diffusion reduces the oxidation resistance of the overlay, and the latter one creates large precipitations and a particle-free zone in the upper layer of the superalloy, causing spalling of the overlay.

In order to reduce the harmful diffusion, a diffusion barrier was developed between the superalloy substrate and the MCrAlY overlay. The work was done as part of a larger project COST 501/II, WP 7A and it was based on the earlier guiding results in the programme COST 501/I. The superalloy used was SSR 99 and the overlay plasma sprayed LC022. The original aim was to reach a lifetime of 4000 hours at 1100°C in air. The developed diffusion barrier consisted of 5 layers, and the total thickness of the barrier was 4.5 μm. The barrier proved to fulfil the original aim and also a similar lifetime at 1150°C.

Other developments for possible future gas turbine blade materials involve a carbon-carbon composite with amorphous carbon matrix with no cracks from production. The density of the material is 1.25-1.35g/cm^3, and the tensile strength at 1500°C is 500-950 N/mm^2. At room temperature the corresponding strength is 400-600 N/mm^2, and the material shows a pseudo-ductility of several per cent.

Applications, Engineering Achievements and Technology Transfer

Most of the mentioned materials development is done as fundamental studies on a laboratory scale, but further development towards engineering application is under way, for example, in the form of collaborative European projects.

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Scientific Key Words: Aluminide coatings; Carbon-carbon composites; Chemical vapor deposition; Physical vapor deposition; Coated and uncoated superalloys; Coating C-C composites; Coating design; Hot corrosion; Palladium/modified aluminide coatings; Single crystal alloys; Superalloys; Thermal barrier coatings; Water vapor oxidation; Zirconia ceramics

Technical Key Words: Engine materials; Aeroengines; Single crystal alloys; Future gas turbine materials; Gas turbines; Thermal barrier coating systems; Surface engineering

SCOPE OF RESEARCH

The main effort of the group is focused on designing and developing high temperature protective coatings (modified aluminide coatings, thermal barrier coatings) in close relation with the industries of the aeronautical sector (engine manufacturers, coating/repairer of gas turbine components) and the energy conversion sector.

The work is linked with basic research studies performed in-house (alumina scale growth, modeling oxidation, hot corrosion of single crystal superalloys and coatings) and in cooperation with university laboratories (University of Nancy, Ecole Nationale Supérieure de Chimie de Toulouse, for example).

Specific Topics

1. Thermal Barrier Coatings

Several topics related to thermal barrier coatings for gas turbine airfoils are being investigated:

a) Growth mechanisms of the alumina layer forming at the interface between the zirconia layer and the bondcoat in order to improve the performance of EBPVD systems (collaboration SNECMA).

b) Modeling the thermal conductivity of thermal barrier coatings in relation with their structure (phases, pores, microcracks, etc.), within the framework of a European project coordinated by SNECMA.

c) Design and development of an equipment for depositing yttria partially stabilized zirconia by PECVD (plasma enhanced chemical vapor deposition) in cooperation with Plasmion and University of Orsay. The laboratory equipment, which permits deposition of YPSZ on MCrAlY is to be upscaled to evaluate the potential of this technique, which represents an attractive alternative to EBPVD and plasma spraying.

2. Pd-Modified Aluminide Coatings

The experience gained in formulating a Pd-modified coating (now commercially available and in service in some engines) is being exploited for developing repair techniques in the case of protective coatings on gas turbine airfoils (collaboration with SNECMA, Sochata, Turboméca).

3. Oxidation and Hot Corrosion of Superalloys

The objective is to understand the influence of addition elements on the hot corrosion resistance of single crystal superalloys (collaboration with Turboméca).

4. Oxidation of Coated C-C and C-SiC Composites

Oxidation of coated and uncoated C-C composites has been modeled. This model, which takes into account the morphological evolution of the material, is being extended for predicting the behavior of other high temperature materials in various oxidizing atmospheres: oxygen, water vapor (with and without hydrogen additions). The corresponding experiments are carried out on a specifically designed oxidation laser bench which permits testing of materials up to 2300 K and under pressures ranging between 0.1 mbar and 5 bars.

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Scientific Key Words: Computer modeling; Corrosion; Oxidation under load; Oxide-metal interface; Surface analytical methods; Water vapor oxidation; Wear

Technical Key Words: Engine materials; Waste incineration; Thermal barrier coating systems; Industrial furnaces; Surface engineering

SCOPE OF RESEARCH

Fundamental Approach

The main topics of research are devoted to the influence of oxygen or gas mixtures on the high temperature properties, such as oxidation or corrosion of metals, alloys and coatings and friction and wear. Many researches are performed to study the role of high temperature oxide scales and coatings in the protection of metals and alloys in oxygen and complex gas mixtures. Specific set-ups are used to analyze the influence of surface treatments and loading on the behavior of oxidized surfaces or coatings, especially with respect to their stress level evolution and/or wear property modifications. In addition to the previous research fields, other research topics are explored based on the diffusion of ^{18}O (as oxygen tracer), microstructural explorations (using transmission or scanning electron microscopy) and surface analyses by nuclear microprobe, secondary ion mass spectrometry and X-ray photoelectron spectroscopy. Moreover, the role of oxide scale on friction and wear at high temperature in oxidizing atmospheres is taken into account; special attention is focused on the influence of water vapor on mechanical properties of oxide scale under surface mechanical loading. The various mechanisms for stress generation in the outer oxide scale, or for mechanical evolution of oxidized samples, are determined by computer modeling in connection with other universities and research centres (ENSAM, Mining School, French and foreign universities).

Applications, Engineering Achievements and Technology Transfer

Applications of these researches are found in every domain where materials are used at high temperature in aggressive environments (power plants, waste incinerators, aeronautical or car industries, nuclear installations). The protective behavior of coated and uncoated surfaces is more particularly explored with respect to their mechanical properties (stress generation, wear or fretting behavior). Collaborations are then established with many academic and industrial centers and particularly aeronautical, military and nuclear centers (ONERA, ETCA, CEA of Saclay and Fontenay aux Roses), electric power industries (especially EDF), iron and steel industries (IRSID, SOLLAC), metallurgy plants (CETIM, IMPHY, St Gobain).

Specific Topics

1. Relation Between Stress Generation and Adherence in Outer Scales (Oxides and Others)

These studies have been done both for oxide scales on Fe-Si alloys and for Al-Si coatings on steels annealed at 500°C and 700°C.

In the first case, a simplified approach to the stress generation was performed using the curvature or "deflection" test in temperature in air. Such a technique helps to determine, for instance, the low stress level which is generated and gives information on the influence of Fayalite on the oxide scale adherence. Further results on the crack propagation into the oxide layers are obtained with the help of a four-point bending test.

In the second case, the coating behaviour is largely disturbed on account of many aliminures phases which are able to form distinctly with respect to the composition of the steel substrate. Also in oxidizing atmospheres, a competition between intermetallic phase transformation and oxide formation is observed, together with interdiffusion processes between coating and substrate. Phases are determined especially using classic and synchrotron X-ray diffraction.

2. Oxidation under Load

Oxidation under load is studied for two distinct systems: NiO on Ni and iron oxides on steels.

In the first system the mechanical behavior is mainly creep. Relations between deformation and oxidation are studied in a specific set-up, which enables creep or stress relaxation measurements in vacuum or in $^{16}O_2$ and $^{18}O_2$ on monocrystalline or polycrystalline Ni. A local analysis of the deformation mechanism is done, based on the "periodic cracking" model of Jobin, Agrawat and Raj. One of the results is the distinct creep behavior of a preoxidized sample with respect to an unoxidized one. Another result is the determination of the evolution of the oxygen diffusion versus applied load and accordingly to the defects in the oxide structure. Nuclear microprobe analysis of ^{18}O is especially used.

In the second system, tensile tests in oxygen of oxidized samples are considered. The study is devoted to the analysis of the mechanical properties of the three distinct iron oxide layers on steels with respect to temperature and steel composition. ^{18}O is used as tracer for the understanding of the oxide scale growth and the stress relaxation phenomena (crack formation, spallation).

3. *Role of Water Vapor on Stress Relaxation in Al_2O_3 Grown on Fe Cr Al Alloy or NiO on Ni*

Without load, the stress level evolution with respect to water vapor evolution is examined in the deflection test and modeling is done using a calculation code (called "Zebulon"). The main influence of water vapor is to modify the oxide morphology and to only decrease slightly the oxidation kinetics of alumina. Also, there is a significant increase in the stress gradient into the whole oxide scale grown in atmosphere containing water vapor with respect to oxygen.

In the case of applied load on Ni/NiO (in creep conditions), a distinct behavior is observed for the outer and inner NiO layers. Particularly the water vapor increases the plasticity of the inner oxide layer.

4. *CO_2 Laser Treatments for Surface Hardening and Elaboration of Protective Sprayed Coating Against Corrosion*

Microstructural, analytical and mechanical approaches are employed to determine the mechanisms of surface hardening of a 551 steel using a CO_2 laser treatment. More specifically, the influence of water vapor thrown on the surface is studied with respect to the thermal effect due to water vaporisation.

When NiCrAlY is prepared from powder thrown on the surface using a CO_2 laser, a distinct oxidation behaviour is noted with respect to a bulk NiCrAlY alloy. Especially, phases containing Y are observed between each laser strand and Y is differently distributed in the outer oxide scale during oxidation as shown by RBS experiments.

5. Oxygen Diffusion Mechanism in Cr_2O_3 Grown on PVD Coating by Using CO_2 Laser

^{18}O isotopic exchange experiments demonstrate that there occurs a preferential diffusion occurs along the grain boundaries of the outer oxide scale. The cationic diffusion was analyzed by oxidation of samples previously covered by a thin layer of ^{54}Cr.

6. Oxidation Mechanism of Fe Cr Alloys with an Al Covering in Front of Liquid PbLi

The study is done to analyze how the oxygen coming from liquid LiPb can effectively help the construction of a thin oxide scale with Al in the coating.

Influences are then expected on the protection of the Al coating in front of liquid PbLi

7. Relation Between Wear and Oxidation

Components of high wear resistance can be obtained with consideration of the tribosystem (environment, loading, lubrication etc) in question by using surface modification technologies and by optimising the microstructure of the materials used. Particularly, the research is focused on wear at high temperature and includes studies about interaction between oxidation and wear. Specifically, one area of activity is the study of large components of ceramic for hot rolling operations in the steel-working industry. In this range, the tribological group has set up a collaborative venture with different European partners in a Brite-Euram project. A special tribometer at high temperature has been designed.

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Scientific Key Words:	High temperature corrosion; Oxidation; Sulfidation; Thermal cycling; Coatings; Reactive element effect; Impurities; Water vapor; Texture; In-situ stress measurement
Technical Key Words:	OMCVD; Sol-gel coatings; Thermo-gravimetry; Vacuum; XRD stress determination

SCOPE OF RESEARCH

Fundamental Approach

The research includes fundamental studies of the transport processes within oxide and sulfide scales (MnS, MoS_2 etc). Co-deposited reactive elements by OMCVD coating are tested for alumina and chromia formers. Attention was placed on the optimisation of the coating process and the effect of the coating on the corrosion mechanism. The method of introduction and the study of the location of reactive elements in oxide and sulfide scales are studied using pure metals, or well characterized alloys, studied as model systems. Fundamental research also concerns the examination of the self crystallographic organisation of corrosion products (Textures) and the influence of the scale texture on the stress level (determined by XRD) in oxide scales and in the substrate. Erosion-corrosion simulated by laser impact studies are also in progress.

Applications, Engineering Achievements and Technology Transfer

OMCVD is to be applied for electronic purposes. Fundamental studies on the role of water vapor, and the presence of alkaline impurities, in the high temperature corrosion behavior of commercial stainless steels have industrial applications.

RECENT PUBLICATIONS

1. High-Temperature Corrosion, Coatings Effects and Characterisation

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5. Buscail, H., Larpin, J.P., Heizmann, J.J. and Laruelle, C., "Influence d'un Dépôt Superficiel d'Oxyde de Cérium sur l'Orientation Cristalline de la Wustite Formées sur le Fer Pur à Haute Température et Basse Pression d'Oxygène," Revue de Métallurgie-Cit/"Sciences et Génie des Matériaux ," 9, 1982 (1994).

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8. Nyassi, A., Larpin, J.P. and Bendriss, A., "Sulfidation Behavior of a Ferritic Commercial Alloy in Different Sulfidizing Environments at High Temperature," Oxidation of Metals, 43, 543-560 (1995).

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10. Buscail, H. and Larpin, J.P., "The Influence of Ceria Surface Addition on Manganese Oxidation at High Temperature," Oxidation of Metals, 43, 237-261 (1995).

11. Bonnet, G., Lachkar, M., Colson, J.C. and Larpin, J.P., "Characterization of Thin Solid Films of Rare Earth Oxides Formed by the MOCVD Technique, for High Temperature Corrosion Application," Thin Solid Films, 261, 31-36 (1995).

12. Buscail, H., Larpin, J.P., Heizmann, J.J. and Laruelle, C., "Influence d'un Dépôt Superficiel d'Oxyde de Cérium sur l'Orientation Cristalline de la Wustite Formée sur le Fer Pur à Haute Température et Basse Pression d'Oxygène," Revue de Métallurgie-Cit/"Sciences et Génie des Matériaux," 5, 661-670 (1995).

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15. Buscail, H., Courty, C. and Larpin, J.P., "Effects of Ceria Coatings on Pure Iron Oxidation. Comparison with Extra Low Carbon Steels," Journal de Chimie Physique IV, Suppl., Vol. III, Coll. C7, 375-380 (1995).

16. Silva, M., Bonnet, G., Larpin, J.P. and Colson, J.C., "High Temperature Corrosion Behavior of Alumina Coated F17Ti Stainless Steel," Book of Abstracts de Euromat 95, Padua/Venice (Italy) 25-28 Septembre (1995).

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21. Courty, C., Buscail, H. and Larpin, J.P., "Effects of Carbon and Manganese Impurities on Cerium Incorporation in Iron Oxide Scales," Journal de Chimie Physique, 93, 1509-1524 (1996).

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Scientific Key Words: Oxidation/sulfidation; Water vapor oxidation; Refractory metals and components; Surface modification/coating; Laser alloying

SCOPE OF RESEARCH

Surface Treatments and Reactivity

The major aims of the work conducted in this group concern high temperature oxidation and sulfidation of metals and alloys, and their reduction by appropriate surface modification or coating application. In order to progress fundamental knowledge, high temperature oxidation processes are studied on their own, as well as surface treatments. When industrial problems of materials degradation are to be combatted, the choice of the right coating solution is therefore made easier.

Specific Topics

1. Fundamentals of High Temperature Oxidation of Dilute Alloys

Concerning the parabolic oxidation of alloys with a low content of a different valence element, we have shown that the Wagner-Hauffe valence approach contains some inaccuracies. We considered the growth of oxides with metal excess or oxygen deficiency and of oxides with metal deficiency or oxygen excess and demonstrated that, in both cases, the evolution of the parabolic rate constant with the impurity content may be not monotonic.

2. Fundamentals of High Temperature Oxidation in Presence of Water Vapor

This underlying research work concerns, at the present date, oxidation of titanium, tantalum, nickel and cobalt. These metals were chosen to represent the most often encountered kinetic laws and oxide morphology. It is tried to understand why vapor inhibits or exacerbates oxidation compared with dry oxygen. In addition to classical kinetic and morphological studies, electrochemical techniques have been shown to be useful as impedance spectrometry and photoelectrochemistry (collaboration with Petit, Dr., LEPMI-Grenoble).

3. Fundamentals of Sulfidation of Transition Metals

As in the case of water vapor, the corrosion of metals by H_2S is not well understood. We studied the sulfidation of tantalum in pure H_2S or Ar/H_2S mixtures. Due to the very low rates, tantalum powder was used to obtain exploitable kinetic curves, showing interface limitation.

4. Surface Alloying by Laser Beam

Many studies are pursued in this field concerning the elaboration of surface alloys mainly devoted to high temperature use in corrosive environments. The substrates studied were two low alloyed ferritic steels (35NCD16 and Z38CDV5). The surface alloys were obtained by laser alloying with predeposits of Cr_3Cr_2 and SiC (on 35 NCD16 steel) and Si, Si_3N_4 or Cr_3C_2 (on Z38CDV5 steel). The oxidation resistance of the treated samples was studied in isothermal and cycling conditions. The formation of a chromia scale was favoured by the initial development of a thin silica film. The surface alloys remarkably resist thermal cycling oxidative conditions at 950°C.

5. Ageing of Silicon Membranes in Ar/Cl_2 Mixtures

The use of silicon membranes in sensors for aeronautic purposes requires the knowledge of their ageing in aggressive environments. Chlorine (without oxygen) leading to volatile $SiCl_4$ seems to be the most dangerous. The reaction of silicon with chlorine being negligible until 200°C, observations are made at higher temperatures and give, by extrapolation, valuable data for the life duration at service temperatures.

RECENT PUBLICATIONS

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7. Caillet, M., De Nicola, M.R., Wouters, Y. and Galerie, A., "Etude Cinétique de l'Oxydation Thermique du Tantale dans des Atmosphères Mixtes Oxygène-Vapeur d'eau," Journal de Chimie Physique, 92, 1142-1153 (1995).

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Scientific Key Words**:** Multilayers; Copper alloys; Nickel alloys; Nickel oxidation; Copper oxidation

SCOPE OF RESEARCH

A Comparison of High-Temperature Corrosion Between Cu/Ni Multilayers and Cu-Ni Alloys with the Same Composition

Stratified deposits are a subject of interest because of their original features (modification of magnetic, structural and mechanical properties, increase in corrosion resistance, etc). The high-temperature corrosion of thick electro-deposited Cu/Ni multilayers, and of alloys with the same composition, has been investigated and compared. For multilayer elaboration, the deposition has been conducted under galvanostatic conditions using a dual-bath technique. The baths have been optimized in order to obtain a planar stratification. Thermogravimetric analysis of the oxidation of these materials between 600°C and 1000°C under 1 atm of O_2 exhibits rates and reaction mechanisms very different from those observed for the alloy of the same composition. The results indicate that products of corrosion are different in the two cases. Considering the reaction mechanisms, the global process of rate-determining diffusion is probably the same for the two kinds of materials but the diffusion paths throughout the scales may be very different. The contribution of boundary diffusion seems to be much more important for the multilayers, taking into account the values of the activation energies. Finally, the multilayer material exhibits a better resistance towards oxidation than the alloy of the same composition, even though it constitutes itself an alloy at the end of the reaction. This is a consequence of the efficiency of the diffusion barrier owed to the growth type of the oxide scales, their plasticity, their adherence and above all to the mode of elaboration of our initial specimens.

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Scientific Key Words:	Electrical heater materials; Superalloys; Impurities; Reactive element effect; Glass-to-metal seals; Preoxidation; Catalyst support systems

SCOPE OF RESEARCH

Main Interests

- High temperature corrosion resistance as a functional property: heat-resisting alloys, electrical heater element materials, superalloys, catalyst support systems.
- Pre-formed oxides for improved bonding in glass-to-metal seals.
- Scale formation during metal processing and its elimination by pickling.

On-Going Projects

- Role of minor additions and impurities on the oxidation behavior of Fe-Ni-Cr and Fe-Cr-Al alloys.
- Effect of impurities and pre-oxidation conditions on the oxide formed on Fe-Ni-Cr glass sealing alloys, and on the quality of the subsequent bond.
- Effect of composition and annealing treatment on scale formation in stainless steels and its elimination by mechanical and/or chemical methods.

RECENT PUBLICATIONS

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Scientific Key Words: Ash; Ceramics corrosion; Chlorine; Flue gas; Hot corrosion; Mixed gases; Mixed oxidants with water vapor; Molten glasses; Molten salts; Nickel alloys; Refractory alloys; Superalloys; Waste incinerator materials

Technical Key Words: Condensate corrosion; Municipal waste-burning; Waste incineration; Nuclear power systems; Industrial furnaces

SCOPE OF RESEARCH

Fundamental Approach

The research includes fundamental studies on the mechanisms of the degradation of alloys and of ceramics in presence of molten glasses or molten salts. Special attention is paid to oxides and oxide layer behaviour.

Nickel base alloys have been particularly investigated in different molten salts, including sodium sulphate and sodium molybdate (with or without molybdenum oxide), and in various atmospheres with different oxygen contents, at temperatures about 1000°C. Mechanisms of the degradation of these alloys have been investigated and the deterious effects of molybdenum oxide has been pointed out and a mechanism proposed.

Engineering Applications

Most of the laboratory work deals with practical solutions to industrial corrosion difficulties in molten glass technology or in waste incineration plants.

Specific Topics

1. Molten Glass Corrosion

The overall aim is to select materials for industrial applications. Tested materials include alloys and ceramics at temperatures between 1100°C and 1450°C. Emphasis is being placed on life-time prediction in relation to glass composition and evolution. The experimental work is done in two facilities where glasses can be handled and added continuously. The flow effect is reproduced in one facility while, in the other one, stresses can be applied to the tested materials immersed in molten glass.

2. Waste Incineration Corrosion

All the aspects of the corrosion in waste incineration plants are investigated : from hot corrosion in various atmospheres at temperatures up to 1500°C, to dew-point corrosion at the condensate temperatures, or with cold walls and different vapor contents in the flue gas, including also specific degradation due to ashes. To achieve the corresponding experimental work, two main facilities are available: the CORALINE facility is designed to operate with toxic gases, various vapour contents and mixed gases. Ash corrosion is simulated in a micro-waste incinerator called CASIMIR which allows generation of real atmospheres resulting from waste burning and taking into account the presence of ashes.

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Most of the work, including fundamental studies (thesis), has been performed with industrial partners and has been reported in internal documents which are confidential.

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Scientific Key Words: Bulk oxide properties; Copper alloys; Copper oxidation; FTIR spectroscopy; Metal/oxide interface; Mixed oxidation states; Nickel alloys; Nickel oxidation; Nonferrous metals; Preoxidation; Surface analytical methods; Superalloys

Technical Key Words: Aeronautical/space propulsion systems; Heat exchangers; Heating elements; Scale adhesion; Solar absorbers

SCOPE OF RESEARCH

Fundamental Approach

Oxides and photon-based analytical techniques are the specialisation of the laboratory.

In the area of high temperature oxidation, work consists essentially of the study of the composition of the high-temperature oxide scales obtained on metals and alloys in air or dry oxygen. The early stages of oxidation receive special focus.

Developments in analysis and surface characterization with infrared absorption-reflection spectroscopy allows the determination of the composition, thickness and structure of the oxide scales. The modeling of infrared reflectance spectra contributes to the enrichment of our library.

The oxidation of copper and copper alloys is of interest both to the scientific and industrial world. Surface analysis by optical methods allows an easy identification of the different copper oxides present in layers from several nanometers up to several micrometers thick.

The roles of various minor alloying additions in austenitic and ferritic steels, nickel-base or iron-nickel-base commercial alloys are correlated with the overall oxidation process.

Applications, Engineering Achievements and Technology Transfer

These are indicated below

Specific Topics

1. *A part of the laboratory's work concerns fundamental studies of practical problems observed in the industrial area:*

   i) corrosion moulds in the glass industry;

   ii) alloy preoxidation in order to develop protective scales;

   iii) failure of electrical contacts in the connector industry;

   iv) surface modification induced by thermal treatment, creating damage such as wearing effects on machine tools in the processing industry.

2. *Another part of the laboratory's work concerns fundamental studies, with the objective to improve specific properties of materials:*

   i) conversion coatings developed on ferritic stainless steels for solar applications, in collaboration with the LME/Paul Sabatier University/Toulouse/France;

   ii) research concerning high temperature oxidation of nickel alloys is being carried out in collaboration with the CEA/Saclay/France;

   iii) the effect of preoxidation of substrates on the formation and adhesion of plasma sprayed coating is being conducted in collaboration with the LMCTS/Limoges University/France;

   iv) work on laser surface alloying of steels for high temperature corrosion/oxidation resistance is being undertaken, in collaboration with the IUC and CAT/Indore/India.

3. *The development of a library of reflectance infrared spectra is being carried out for several incidence angles and different oxide layer thicknesses, oxide layer compositions and oxide layer structures.*

4. *The surface analytical methods available are the following: low-angle X-ray diffraction; electrochemical measurements; Mössbauer spectroscopy; UV-Vis-NIR spectroscopy; FTIR spectroscopy; photoluminescence spectroscopy; SEM-EDS. XPS, RBS and X-ray absorption spectroscopy are complementary techniques available in IPN/Lyon University or LURE/Orsay University.*

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Scientific Key Words: Coal-ash corrosion; Combustion gases; Deposits; Heat-resistant steels; Steam-side corrosion

Technical Key Words: Coal-fired boilers; Waste incineration

SCOPE OF RESEARCH

Fundamental Approach

The research objective is to give an answer to two main industrial problems, namely (a) to determine the corrosion rate of a given metal in given corrosive media at a given temperature and (b) the relationship between the variation of this rate and the chemical and metallographic composition of this metal. This requires other studies to determine the corrosion mechanisms, e.g involving diffusion, heterogeneous reaction kinetics, thermodynamic equilibria calculations. Studies are generally based on samples exposed in appropriately prepared laboratory furnaces and evaluation of results is by TG, metallographic and corrosion products analyses. Results and their interpretation are compared with the in-situ behaviour of materials and bibliographic data.

Applications, Engineering Achievements and Technology Transfer

Specific Topics

1. *High Temperature Corrosion Studies of Heat-Resistant Steels in Gas Mixtures and in Contact with Aggressive Solids*

The object is the determination of the resistance and the corrosion mechanisms of steels used for tubes in pulverized coal thermal power stations, normally the Cr10 Mo1 type, such as T91, EM12, X20. Therefore, the corrosive media studied simulate combustion gases (O_2, CO_2, SO_2, H_2O, N_2 etc) and deposits coming from fly ashes. The results are evaluated with gravimetric, metallographic and microscopic methods and surface microanalysis.

The results obtained are collected in the report of E.N.S.T.I.M.D. Study of the EM12, T91, X20 corrosion of steels by pulverized coal, which belongs to Vallourec Industries.

2. High Temperature Corrosion Studies of Heat Resistant Steel in Water Vapor

The purpose is the determination of the corrosion rate of heat-resistant ferritic steels, such as Cr10 Mo1 grade, in vapor generator systems. The study is based on the determination of corrosion rate by TG measures and microscopical observations in the temperature range of 500-700°C. This study is running and is planned to end in 1997.

3. High Temperature Corrosion Studies in Waste Incinerator Gases

The aim of this research is the determination of corrosion kinetics and mechanisms of low alloy steels (Cr2 1/4 and Cr10 Mo1 grades) in waste incinerator atmospheres. Tests are conducted in 9% O_2, 15% H_2O, 0 a 3000 ppm HCl, the balance being N_2 atmospheres, in the temperature range 300-600°C. Evaluation of resultsis made by TG, metallographic and corrosion products analyses. This study will end in 1997 and is presented as a doctoral thesis.

4. Fundamental Research About Self Diffusion and Points Defects (Ionic and Electronic)

This is undertaken with chromium oxide, Cr_2O_3, which is pure and nickel (or NiO) and titanium (or TiO_2) doped, in the range of temperatures, 400°C-1200°C (752-2192°F). The investigation techniques used are the measurement of the electrical conductivity in terms of temperature and oxygen partial pressure, measurement of Cr^{51} tracer selfdiffusion and chromium selfdiffusion in an electrical field. The interpretation of the results is made with regard to the generalized Nernst-Einstein relation and the Kröger & Vink method related to the function, point defects concentration—pO_2.

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Scientific Key Words: Alumina; Chromia; Diffusion; Transport in scales and bulk oxides; Reactive element effect; Impurities; Metal/oxide interface; Residual stress; Strain measurements; Stresses and scale behavior; Creep-oxidation interaction; Modeling

Technical Key Words: Aerospace systems; Electrical resistors; Surface engineering

SCOPE OF RESEARCH

Oxidation Mechanisms

This research is in relation to transport phenomena in oxide scales and the influence of impurities and active elements.

Several parameters can be considered:

1. Influence of the Substrate Structure, of the Oxidation Conditions, etc...

(a) As Gesmundo, F., came for one year to the laboratory, a study of the high temperature corrosion behaviour of two-phase Cu-Ag alloys was developed. The aim was experimentally to verify the theory previously developed by Gesmundo on the corrosion behaviour of two-phase alloys and to relate the structure of the inner oxidation zone to the diffusional parameters and to the respective amounts of each element in the alloy. (Papers 9 and 12). See also paper 3 on the effect of microstructural defects.

(b) This work on the effect of a laser beam was developed in collaboration with ETCA (Arcueil, France) on chromium coatings (see papers 1,2,4 to 7), and the thesis of S. Beauvais-Réveillon. The oxidation kinetics are enhanced only at the beginning of the oxidation and the nature, morphology and composition of the scale are not modified when compared to classical oxidation. Self-diffusion coefficients in the chromia scale were also measured but, using Wagner's theory, the calculated oxidation constant is smaller than the experimental one.

(c) The effect of pO_2 on chromia growth on Ni-30Cr was studied. (See thesis of Tsaï, C.S., and paper 27.) It was observed that such chromia scales behave as a p-type semi-conductor, in a pO_2 range 0.1-2 atm. This is in favour of $O_i^{''}$ or/and $V_{Cr}^{'''}$ point defects. However, the variation law could not be determined as the pressure range is too small.

2. Effect of Impurities and Doping Elements

(a) Influence of Si on the growth of chromia scales (on a stainless steel). See paper 10.

The oxidation kinetics are not significantly modified, even with large amounts of Si (up to 5%) and over a large oxygen pressure range (0.21 atm to 10^{-10}atm). Even by accurate XPS analyses, a continuous layer of SiO_2 was never evidenced. The silicon effect mainly consists in avoiding the incorporation of nickel and iron.

(b) This relates to the effect of active elements on the oxidation mechanism. First, an electrochemical method was used, simultaneously, to more classical experiments, in the case of alumina scales developed on βNiAl (J. Balmain's thesis and papers 11 and 14). It is based on the determination at high temperature of characteristic intensity-potential curves I(V) for alumina scales at various pO_2. It appeared that yttrium slightly decreases the oxidation kinetics and slightly increases the scale adherence. This is related to the fact that yttrium is incorporated in the inner part of the scale, avoids the incorporation of Ni in alumina scale and decreases the aluminum outward diffusion. A similar effect of yttrium is found for chromia scales developed on Ni-30Cr (Papers I-8,11,13 and Tsaï's thesis).

The effect of yttrium (and other doping elements) is also studied on the oxidation of FeCrAl alloys. (Paper 11 and Messaoudi's thesis). With such alloys, the effects on the oxidation kinetics can largely vary according to the elaboration mode of the alloy and its purity degree. However, this work on the role of active elements is mainly focused on their influence on the stress generation during oxidation sequences and on the stress elimination by creep.

3. First Stages of Oxidation: "In-Situ" Approach by XPS

This part is in progress (see paper 11) and the objective is to determine the nature of the scale as it is formed on a heating stick in the XPS chamber. Up to now, some experiments have been performed on steels, at low oxygen pressure up to 500°C. During the heating in ultra-vacuum, there is a modification of the chemistry of the sample surface (precipitate dissolution and associated segregation phenomena).

Transport in Oxides
Microstructure and Microchemistry

1. Transport in Oxide Scales. Comparison with Transport in Bulk Oxides

In the past years, many self-diffusion studies have been performed by the group on chromia and alumina bulk oxides (see previous work of Sabioni et al. and papers 17-21, 24-26, 28,30,34,35. It was always observed that such self-diffusion coefficients could not justify the oxidation rate of chromia- or alumina- former alloys: the calculated oxidation constants (on the basis of diffusion coefficients) were always smaller than the experimental oxidation constants. In this last period, attempts were made to explain this discrepancy and to develop self-diffusion measurements directly on oxide scales. Nevertheless, as yttrium is frequently used, its diffusion in bulk alumina and in chromia scales was also studied.

(a) An important work was performed concerning self diffusion in chromia scales formed on Ni-30Cr (see Tsaï's thesis and papers 23,27,28,29,32,39,40,41). At 900° and 800°C, the growth mechanism of Cr_2O_3 scales was studied by determining the diffusivities, in the bulk and along grain boundary, of ^{18}O and ^{54}Cr in Cr_2O_3 scales formed on a $Ni_{70}Cr_{30}$ alloy unimplanted and implanted with yttrium (10^{16} ions/cm^2). The diffusion of ^{18}O and ^{54}Cr was carried out simultaneously, which allowed a direct comparison of self-diffusion to be obtained. All the concentration profiles were established by SIMS.

Two important modifications were made in comparison of the classical analyses of the penetration profiles:

(i) the first part of the penetration profiles was attributed to apparent diffusion (instead of bulk diffusion) and the second one to grain boundary diffusion,

(ii) the 'f' value, fraction of sites associated to grain boundaries, was modified taking into account the roughness of the scale surface.

With these two modifications, a good agreement is then observed between self-diffusion coefficients determined in polycrystals and those determined on scales.

Without yttrium in Cr_2O_3 scales, the oxygen bulk diffusion coefficient is close to that of chromium, but the chromium grain boundary diffusion coefficient is greater than that of oxygen. The presence of yttrium in Cr_2O_3 scales slightly decreases the grain boundary diffusivities of ^{18}O and ^{54}Cr, but enhances oxygen lattice diffusion.

The parabolic oxidation rate constants calculated from the diffusion data according to Wagner theory are now close to the experimental ones determined by oxidation kinetic tests.

It is concluded that the Cr_2O_3 scale growth is controlled by counter-current diffusion of oxygen and chromium for the unimplanted and implanted alloys, mainly by grain boundary diffusion. Yttrium does not change the growth mechanism.

(b) Similar studies were conducted in alumina scales developed on βNiAl (see Balmain's thesis and papers II-31,36,37,40,43).

The diffusion treatments were performed at 1100°C by $^{18}O_2$ isotopic exchange and cationic self-diffusion was simulated by chromium diffusion. Though the analysis of the penetration curves was modified as stated before, the diffusion coefficients determined thus do not agree with the parabolic oxidation constants. These discrepancies are related to the fact that the diffusion coefficients are determined only in the outer part of the scale and that, for cationic diffusion, the cationic chemical potential gradient is opposed to the diffusion flux. Moreover, the alumina scales are not as compact as the chromia scales.

Using the electrochemical method, it appears that the calculation of the parabolic oxidation constant deduced from the ionic conductivity evolution in the scale leads to a value close to that of the experimental value. This good agreement, contrary to the previous comparison, is probably due to the fact that, in this last case, 'atomic' transport phenomena in the whole scale thickness are taken into account. Moreover, such a technique allows determination of the evolution of parameters such as the oxygen chemical potential throughout the scale, or the ability to plot the evolution of any other parameter (for instance the concentration of an impurity) as a function of the oxygen chemical potential in the scale.

(c) A similar study on alumina scales formed on various FeCrAl alloys is in progress (Messaoudi's thesis). The agreement between calculated oxidation constants and experimental ones depends on the quality (compactness, crystallinity) of the alumina scale. If the scale has a low degree of compactness, as for the scale formed on β NiAl, then the comparison of the two types of oxidation constants is not at all satisfying.

(d) Yttrium diffusion in α alumina single and polycrystals (see papers 17 and 44). Results show a very low penetration depth in bulk and a great one along the short circuits. The difference between D_b and D_{gb} is particularly important: $D_{gb}/D_b \approx 10^8$. This is correlated to the low solubility limit of yttrium in alumina and its strong segregation along short-circuits, dislocation walls and grain boundaries.

(e) Yttrium diffusion in chromia scale (see paper 45).

The results show that yttrium, probably on account of its large size, diffuses slightly slower than chromium in the bulk and along grain boundaries of chromia scales. The activation energy of grain boundary diffusion is greater than that of bulk diffusion, probably due to interaction effects between the diffusing species and the impurities in the grain boundaries.

The difference between bulk and grain boundary diffusion coefficients for yttrium is smaller than in the case of yttrium diffusion in alumina. It is suggested that the difference of yttrium grain boundary diffusion in Al_2O_3 and Cr_2O_3 is related to a greater solubility of yttrium in chromia than in alumina, and, as a consequence, to a stronger yttrium segregation along grain boundaries of alumina.

2. Microstructure and Microchemistry of Doped Al_2O_3. Local Order Around the Doping Elements (Papers 16,22,33,38,42)

In order to clarify the mechanisms by which yttrium or other active elements act on the growth kinetics of alumina, studies of the microstructure and microchemistry associated to a study of the local disorder around the doping element (EXAFS) are performed. Alumina is doped either with Y_20_3, zirconia or palladium by sintering.

(a) In case of yttrium doping, for samples with an yttrium amount higher than > 0.03% mol Y_20_3, most of the yttrium is precipitated as $Y_3A1_5O_{12}$. The apparent solubility limit of yttrium at T = 1550°C is close to 0.03% mol Y_20_3. However, yttrium is mainly segregating in grain boundaries, with $C_{gb}/C_b \sim 50$. So, the solubility limit in the bulk has been estimated as ~ 10 ppm at 1550°C. For low doping amount, (0.03% mol Y_20_3) most of yttrium is situated on cationic sites and, due to the great size of yttrium atoms compared with aluminium atoms, defect complexes are created as it follows:

$$Y_{Al}^{x} \Leftrightarrow \left(Y_{Al}^{x} + mV_{O}^{\cdot\cdot} + nO_{i}^{''}\right)^{2(m-n)\cdot} \quad \text{with } m > n$$

These defect complexes behave as donors.

It was also shown that the solubility of yttrium is increased by a decrease of the oxygen pressure. Alumina grain growth is limited by yttrium segregation and precipitation along grain boundaries and the mechanical properties of alumina are improved when yttrium is either in solid solution or segregated. The garnet phase precipitation decreases the alumina toughness.

(b) Contrary to yttrium, palladium does not segregate along grain boundaries and its solubility is smaller. It forms a metallic phase of Al_xPd_{1-x} (x~3/5). The XAS study at the K-edge of zirconium and chemical analyses on thin foils of Zr-doped alumina indicate that zirconium atoms have a strong tendency to localize in alumina grain boundaries. The enrichment ratio depends on the alumina grain size. For an average grain size of about 3.5 μm, the segregation ratio is $C_{gb}/C_d \sim 8\ 10^{-3}$. In the grain boundaries, Zr-ions form little nanometric oxide clusters whose structure depends on their size, i.e. on the segregation ratio. For a small size of such clusters, the contribution of the free surface energy becomes preponderant and the tetragonal phase of zirconia, which is the allotropic phase stable at high temperature, becomes stable at room temperature.

Stress Analyses in Oxide Scales

In order to characterize the respective importance of growth stresses, thermal stresses, and stress relaxation, a high temperature chamber for X-ray diffraction was designed some years ago in ENSAM, Paris, allowing to work in controlled atmospheres, using the $\sin^2\Psi$ method. In a first step, the system Ni/NiO was chosen as only one oxide grows and its oxidation behavior is well known. Residual stress analyses were performed both at high temperature and at room temperature on nickel samples previously oxidized at 900°C (see papers 46-53).

In this last period, the work was focused on the stress determination in NiCr/Cr_2O_3 system and on modeling (papers 54-56 and Daghigh's thesis).

High temperature X-ray diffraction has been used first for measuring the expansion coefficients of Ni-30Cr alloy and Cr_2O_3 between 20 and 900°C.

Then, the stresses created in the chromia scale formed on NiCr were determined as a function of various parameters: substrate and oxide scale thickness, grain size, yttrium doping, cooling rate. Besides, relaxation phenomena have been experimentally observed during isothermal or anisothermal heat-treatments after previous oxidation at 900°C.

After oxidation, the stresses in the oxide scale are compressive, their value decreases with the annealing temperature or time and they tend to zero at 900°C, indicating that the oxide growth stresses are negligible.

During heat-treatment after a previous oxidation, it is possible to eliminate the stresses. The relaxation by creep depends on the temperature and on the presence of yttrium. No relaxation is observed for small temperatures and stress relaxation is promoted by yttrium.

Simultaneously, a numerical model was developed to describe the stresses and the relaxation phenomena. It takes into account the mechanical behaviour of the substrate and of the oxide scale and solicitation parameters such as the cooling rate or the heat-treatment duration, etc. This elasto-visco-plastic modeling agrees with the evolution of experimental results with the various parameters of the study.

By now, X-ray diffraction is used for determining stresses in alumina scales formed on FeCrAl alloys (Messsaoudi's thesis in progress). The more or less important values of compressive stresses in the scale found at room temperature are correlated to the alumina scale morphology and to the oxidation resistance.

In Progress

- Study of the first stages of oxidation or of thin films by an "in situ" approach in XPS
- Analysis of kinetic curves which follows a complete law: $t = \frac{1}{k_l} x + \frac{1}{k_c} x^2$
- Study by TEM and Analyses of Metal-Oxide Interfaces and Oxide Scales. Effect of doping elements on the morphology
- Relation between Stresses and Adherence of Oxide Scales

  (a) Stress determination by XRD, by RAMAN and by deflection

  (b) Stress relaxation

  (c) Stress modelling
- Local order around doping elements in grain boundaries of alumina

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THESES

S. Beauvais-Réveillon 1994
"Oxidation of a Chromium Coating on Various Substrates. Comparison of the Oxidation Mechanisms in a Furnace or Assisted by a Continuous CO_2 Laser at Constant Temperature".

J. Balmain 1995
"Transport Properties of Alumina Scales Developed on β NiAl. Influence of Yttrium and Palladium Doping".

C.S. Tsaï 1996
"Relation Between Self-Diffusion and the Growth Mechanism of Chromia Scales. Influence of Yttrium Doping".

S. Daghigh 1996
"Stress Evolution in Ni-30Cr/Cr_2O_3 System as a Function of Temperature. In-Situ Study by X Diffraction and Modeling".

THESES in Progress

K. Messaoudi
"Resistance of Alumina Scales Formed on Various FeCrAl Alloys. Stresses Associated to the Oxidation".

G. Calvarin
Collaboration with E. Andrieu and R. Molins, ENSMP. "Microstructural and Mechanical Aspects of the NiCr-Cr_2O_3 System During Oxidation of Thin Foils".

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Scientific Key Words: Alumina growth; Auger electron spectroscopy; Coated and uncoated superalloys; Ceramics/molten aluminium; Internal oxidation; Plasma coatings; Refractory alloys; Composite interface reactions; Creep/fatigue-oxidation interactions; Metal/oxide interface; Microstructural analysis; Nucleation; Nickel alloys; Superalloys; Transmission electron microscopy

Technical Key Words: Gas turbines; Single crystal alloys; Conventionally-cast alloys; Ceramic components; Zirconium alloys; Wear resistance; Thermal barrier coating systems; Nuclear power systems; Heat exchangers; Catalyst support systems; Steam generators; Engine materials

SCOPE OF RESEARCH

Fundamental Approach

The high temperature corrosion aspects are found in many of the Materials Center research topics concerning high temperature materials, metals, composites, intermetallics and ceramics. Oxidation, decarburization, hydration and liquid metal interaction are given special attention. The approach covers a wide range of scales since TEM analysis of the first stages of high temperature oxidation is performed and corrosion products a few mm in thickness are studied. The temperature range of interest is from 350°C (nuclear power generation system) to over 2500°C, also for nuclear engineering (management of the interaction of the molten core with refractories in the event of a major accident). Environmental effects and associated microstructural evolutions on the mechanical behaviour of various materials are studied.

Thermodynamic aspects of corrosion, as well as kinetic aspects, are considered. The studies are applied rather than fundamental since work on model systems is rarely undertaken, corrosion is also rarely studied as such but usually in conjunction with mechanical behaviour and with mechanical damage.

Applications

The applications are in the field of energy conversion systems: nuclear power generation, aeroengine turbines, internal combustion engine. All the research is carried out under contracts from industry, government or EEC agencies. With the development of a plasma processing center in association with Ecole des Mines and other local partners, it is now possible to deposit coatings under various conditions ranging from low partial pressure to high pressure (4 atm).

A non-exhaustive list of subjects with a significant share of corrosion studies follows:

1. Metallic FeCrAl Substrates for Catalytic Converters

These materials (50 to 100 μm thick foils) have to withstand temperatures of the order of 1200°C under rather oxidizing conditions. The alumina layer is adherent and the oxidized material which may be considered as a composite (alumina/Fe-Cr steel) exhibits thermal ratcheting. The oxidation behaviour of thin FeCrAl strips between 800°C and 1200°C is investigated in relation with kinetic studies. The different observed kinetic regimes are correlated to oxide morphologies themselves related to different oxide structures (transition γ platelets and stable α alumina). The positive effect of active elements has been demonstrated. The structure (honeycomb type or corrugated) is brased locally with nickel-based brazes, with the effect of turning a ferritic material into an austenitic one.

2. Thermomechanical Fatigue of Materials Used in Aeroengines

Fatigue and crack growth in high temperature metallic or MMC materials are studied through an approach combining a detailed mechanical study and a microstructural study of damage to lead to life prediction under various environments. Anisothermal low cycle fatigue tests simulate thermomechanical fatigue of turbine blades. Directionally solidified (single crystals) materials may be protected from corrosion by various coatings. Oxidation of uncoated materials is affected by microstructural features (interdendritic spacings, or the size of carbides).

3. Nickel Base Alloy Intergranular Embrittlement in Relation with Oxidation Mechanisms

The purpose of this study is to specify the parameters which are responsible for the oxidation assisted intergranular embrittlement of nickel-base alloys. Creep-fatigue crack growth tests have been conducted on Ni-Cr alloys and superalloys at 650°C and under a range of oxygen partial pressures (10^{-9} to 0.2 atm). These tests give evidence of a sharp increase in the fatigue crack growth rate beyond a transition pressure. The transition pressure is independent of mechanical parameters, such as the loading amplitude and the frequency but depends on the chromium content and is, furthermore, linked to the oxidation mechanisms identified by using analytical TEM. Other tests have been explored, superimposing a square wave pressure on either side of the transition pressure to mechanical cycles. These experiments lead us to conclude that the embrittling process is a very local phenomenon, linked to nickel oxide formation and the stress relaxation ability of the material.

4. Corrosion of Ceramic Tubes Immersed in Aluminium Foundry Baths

Silicon carbide based ceramics are preferred for heat exchanger type of applications (immersed burners). The damage occurs primarily when flux covers are used and materializes by the reaction of Al with silicon nitride (the binding phase) to form AlN, or with graphite (a second binder phase) to form aluminium carbide. A corrosion mechanism has been proposed which rests on the formation of volatile halides permeating through the porosities at the metal/flux/ceramic triple junction and transporting Al deep into the material.

5. Interaction of "Corium" with Refractories in Nuclear Reactors

In the case of a severe incident, the core and the materials it contains may melt and be poured over the underlying refractories. Thermodynamic and solidification calculations suggest the corium separates into a ceramic (uranium- and zirconium-rich) part depositing at high temperature (>2400°C) and into a metallic part which may end solidifying at 1500°C or below. Experiments are conducted to study the interaction of the liquid metallic component with the refractories that are candidates for the application.

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Scientific Key Words:	Alumina growth; Ceramic coatings; Growth stress; Oxidation under load; Refractory alloys; Plasma coatings; Residual stress; Thermal cycling
Technical Key Words:	Engine materials; Thermal barrier coating systems; Hot gas filtration; Heating elements

SCOPE OF RESEARCH

1. The first theme of this research is the influence of the composition and the elaboration mode on the oxidation mechanism, especially on adherence and spalling of the oxide scale. These two factors are dependent on the mechanical properties of both material and oxide scale. So, the mechanical properties of the material were studied to correlate their evolution with the modification of the oxidation behavior. The second theme of this research is the influence of the mechanical stresses on the oxidation behavior of the material. The mechanical stresses can be residual stresses coming from the elaboration mode of the material, or external stresses as it will occur when the material is on duty in a machine, or in a device. The growth stresses in the oxide scale are also very important since they can cause the breakdown of the oxide scale if they are very high. Thermal stresses can also damage the oxide or coatings in thermal cycling conditions.

2. Two types of material were studied: an alumina forming alloy and a ferritic alloy, coated with metal or zirconia.

Applications and Engineering Achievements

1. Influence of the Composition and the Elaboration Mode on the Oxidation of FeCrAl Alloys

This study was developed with the EDF- GDF Research Center Les Renardières of Moret sur Loing, France (Clemendot, F.). The industrial materials are made by casting, or by powder metallurgy. The aim of the work was to explain the changes coming from the presence of yttrium, or the fabrication process, in air oxidation conditions.

2. Influence of Mechanical Stresses on the Oxidation of an FeCrAl Alloy Coated (FeCrAlY, Zirconia) or Non-Coated

The work on the influence of stresses on the FeCrAl alloy oxidation was undertaken with the EDF-GDF Research Center Les Renardières (Moret sur Loing - France) . It was also the theme of the Commission "Corrosion by hot gases" of the CEFRACOR. The determination of residual stresses in thin alumina scales is carried out at room temperature and at high temperature (collaboration with the "Institut de Science et de Génie des Matériaux et Procédés", Odeillo, Font - Romeu, France) to correlate the stress levels (growing and thermal) to the behavior of the alloy and the morphology of the oxide scale. The coatings were tested in thermal cycling conditions and their resistance to damage is explained.

RECENT PUBLICATIONS

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Scientific Key Words: Ceramic ageing; Ceramic elaboration; Semiconductor oxidation; Diffusion; Electrical conductivity; Electrochemical measurements; Impurity segregation; Interfacial effects; Metal/oxide interface; Point defect effects; Sensors; Thermodynamic/defects of oxide solid solutions; Zirconia ceramics; Uranium oxide; Perovskites

Technical Key Words: Membranes; Ceramic components; Electrochemical microsensors; Sintering

SCOPE OF RESEARCH

Fundamental Approach

The work concerns the study of atomic transport and diffusion processes in multicomponent oxides exposed under a generalized thermodynamic potential gradient. A directed diffusion of the various components takes place in the material by way of defects. This can lead to cation redistribution (kinetic demixing) in the sublattice, when species with different mobility participate in the transport processes.

A part of the work is also devoted to the study of the defect properties and to the determination of diffusion coefficient in ceramics. Their knowledge is of great importance both to understand and to predict the behavior of multicomponent oxides under non-equilibrium conditions.

Applications, Engineering and Technology Transfer

Cation or anion redistributions can alter the kinetics of growth of an oxide scale on an alloy and the mass transfer across the oxide/metal interface. Such effects are also an important cause of ceramic deterioration at high temperature.

Specific Topics

1. *Alloy Corrosion*

The work concerns the influence of the cation redistributions on the kinetic of growth of the corrosion scale and on the advancement of the oxidation front in the metal.

2. *Ageing of Ceramics*

Ageing of ceramics, such as doped-zirconia, under an electrical field or subjected to a nonhydrostatic state of stress is being studied.

Ageing of ceramics, such as alumina or transition metal oxides, under the influence of a temperature or a chemical potential gradient, is also a subject of research.

RECENT PUBLICATIONS

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2. High Temperature Degradation

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Scientific Key Words:	Coatings/graded layers; Creep/fatigue-oxidation interactions; Interfacial effects; Metal/oxide interface; Role of interfacial reactions; Surface modifications; Thermal barrier coatings
Technical Key Words:	Gas turbines; Single crystal alloys; Thermal barrier coating systems; Nuclear power systems; Surface engineering

SCOPE OF RESEARCH

The main goal of the research is to analyze the role of interfacial reactions in the oxidation behavior and resistance of high temperature materials. Indeed, the growth of an oxide scale, or any other corrosion product, is always a combination of mass transport (diffusion) and mass transfer (interface reaction) processes,so that the rate of the slowest step determines the initial scaling rate. At high temperature, interface reactions are too fast and diffusion is usually the rate-limiting process but, at intermediate temperatures, the rate of interface reactions can be sufficiently slow to participate in the control of the oxidation/corrosion kinetics. Therefore, a detailed study of the transfer processes at the interface would lead to a better understanding and control of oxidation and corrosion at intermediate temperatures. The role of mechanical deformation, substrate microstructure and surface preparation or modification on scaling kinetics is also investigated.

Specific Topics

1. Role of Interfacial Reactions

From an analysis of mixed kinetics (interfacial and diffusional), the reactive element effect (REE), as observed for chromia scales, was interpreted as a blocking of one of the cationic interface reactions. This model of REE was extended to a pure metal like nickel. The segregation of Ca, Sr or Ba oxide at the NiO-Ni interface was found to induce a decrease of one to two orders of magnitude in the oxidation rate of nickel and a drastic change in the microstructure of NiO scales. This strong effect of alkaline-earth elements on the oxidation of nickel can apparently be interpreted by an inhibition of interfacial reactions.

2. Interactions Between Oxidation and Deformation

For many materials, a large change in crack growth rate is observed at a critical oxygen partial pressure. The phenomena associated with such a threshold in P_{O_2} were carefully analyzed. In the case of nickel-base superalloys, the critical P_{O_2} corresponds to a transition between the growth of a chromia scale and the growth of a scale containing large amount of NiO. Therefore, the interfacial reactions involved in the nucleation and growth of differing oxides at the tip of a propagating crack appears to have a quite large influence. This work was performed on alloy 718, single crystal superalloys and binary Ni-Cr alloys.

3. Oxidation of Complex Alloys

The oxidation behavior of many different alloys was studied. The most recent works deals with single crystal superalloys and Nb-Ti-Al alloys. The aim of these studies was to determine the role of alloy composition and microstructure on scale growth mechanisms and kinetics and on scale properties (composition, morphology, microstructure, adherence). In addition, for single crystal superalloys, the behavior of the oxide scale during cooling was particularly investigated and, for Nb-Ti-Al alloys, slight improvement in scaling behavior was achieved through the use of specific ‘dopants’ acting on interface reactions.

4. Thermal Barrier Coatings

The influence of the structural and chemical characteristics of ceramic (PSZ) and bond coat (MCrAlY) powders on the microstructure, properties and thermal cycling behavior of plasma-sprayed TBC was investigated. For a given set of projection parameters, the volume fraction of tetragonal zirconia, the morphology and granularity of PSZ powder and the aluminium content of MCrAlY are the most important parameters for the resistance of TBC to thermal cycling.

5. Surface Modifications

Surface modifications by means of chemical conversion treatments and electrolytic deposition of oxide are studied to see how they induce a controlled change in surface morphology, composition and microstructure. The goal of these treatments is to get a graded conversion scale adherent to the substrate such as steel, stainless steel, or superalloys, to improve their resistance to high temperature oxidation or corrosion, or to improve the adherence of ceramic coatings.

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6. Oxidation of Complex Alloys

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Scientific Key Words: Hot corrosion; High temperature oxidation; Coatings; Glass melting; Refractory alloys and compounds

Technical Key Words: Gas turbines; Waste incineration;

SCOPE OF RESEARCH

Fundamental Approach

When used at high temperature, refractory materials must satisfy two stability criteria, from the structural and physico-chemical point of view. As regards the first one, bulk and coated materials are concerned. So an important part of research must be devoted to structural as well as diffusion studies, so as to define thermally stable alloys or coating/alloys systems. This point has been studied in the case of refractory base alloys and also of nickel base superalloys/coatings systems.

As far as physico-chemical stability is concerned, research in this field have been focused on high-temperature oxidation in air or multi-oxidant gases (O_2-SO_2, O_2 - HCl , O_2 - SO_2 - HCl) and hot corrosion. In this latter case, several types of (molten) condensed phases have been studied, the common characteristic of which is the presence of oxo-anions. It is thus possible to describe hot corrosion reactions with use of the classical redox/acido-basicity formalism. This is particularly interesting in the case of molten glass, where a complete study has been undertaken to determine the corrosion mechanisms of Ni-Cr alloys.

Applications, Engineering Achievements and Technology Transfer

a) Hot Corrosion of Refractory Alloys Used in Gas Turbines

The aim of this research is to try developing new alloys or coatings which could enable turbine blades to resist for a long time hot corrosion due to molten salts (sulfates), and high temperature oxidation. Niobium-based alloys and Pd-containing aluminides are being studied with this goal.

b) New Alloys Used in the Glass Industry

Glass melting processes, especially fiberglass manufacturing and vitrification of nuclear waste , suffer from temperature limitations due to corrosion of metallic materials by molten glass. The aim of this research is to develop new alloys which could be used for a longer time at temperatures about 1000°C, or resist to temperatures exceeding 1300°C.

c) Materials for Waste Incineration

Waste incineration (industrial or domestic) produces very corrosive atmospheres which drastically limit the lifetime of metallic materials used for making tubes, grids, etc.. The aim of this research is to characterize the corrosion processes, so as to propose new materials resisting to these severely corroding conditions.

Specific Topics

1. Pd Modified Aluminide Coatings

Palladium is a good alternative to platinum in order to modify aluminide coatings used to protect superalloys against oxidation and corrosion. Coating processes, the Ni-Pd-Al phase diagram and diffusion in this ternary system are being studied, in order to propose a complete description of the mechanism of aluminization of Pd-precoated superalloys. The work is in partnership with ONERA and SNECMA

2. Corrosion of Alloys by Glass Used for Fiberglass Manufacturing

Ni-Cr alloys used for fiberglass manufacturing suffer from high-temperature corrosion, and must be modified to increase their lifetime. Mechanisms of corrosion are being studied, in order to propose adequate modifications: alloying elements, surface treatments. New alloys are also being studied. Partnership is with Isover Saint Gobain and Saint Gobain Ceramics (USA).

3. High Temperature Materials used in Waste Incineration Plants

Study of the corrosion processes of alloys, coatings and refractories (silicon carbide, alumina) used in waste (municipal and industrial) incineration plants, is being undertaken. Partnership is with Stein Heurtey and Rhone Poulenc.

4. Protective Coatings for Niobium Alloys

Study of a pack cementation process capable of producing complex silicide coatings for niobium alloys, which offer significant promise in oxidizing environments to the highest temperatures of their application, is under way. Partnership is with Dassault, CNES and CEP.

Research Facilities

Thermogravimetry Equipment

5 thermobalances for high temperature studies with corrosive atmospheres (SO_2, HCl, CO-CO_2).

Synthesis Equipment

2 HF furnaces (30 and 50 KW) for melting high temperature metallic materials

1 high temperature furnace (1700°C) with pressure equipment (10 T) for sintering

planetary high energy ball milling machines

laboratory vacuum equipment for annealing and synthesis

High Temperature Electrochemistry

5 computer driven potentiostats

2 frequency analysers for impedance measurements

Analysis

2 microprobes (CAMECA)

2 scanning electron microscopes (HITACHI, PHILIPS) with EDS analysis

6 X-Ray diffractometers

1 transmission electron microscope (Transmission: 200 kV)

Partnership with Abroad

Present Partnership

NORTHBORO Research Center - NORTHBOROUGH - MA (USA)

ATOCHEM USA

Desired Partnership

Themes: materials and coatings for high temperature applications (gas turbines, incinerators, glass melting)

Competence: high temperature oxidation and corrosion, electrochemistry, surface analysis.

RECENT PUBLICATIONS

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SCOPE OF RESEARCH

Unfortunately, the group has not carried out full-scale research studies, because of the well-known events in the country in recent years. Extreme material and technical hardships, and an information vacuum, forced the group to halt the activities of the team. However, the chance is taken here to present the plan of the team for the future activities, that cannot be fulfilled yet because of lack of funding. The possibility of joint research with other laboratories is raised.

1. Areas of Interest

The general aim is to determine the crystallographic and structural regularities of oxide layer development (nucleation and growth) on refractory metals and alloys during high-temperature metal-oxygen reactions of free and latent surfaces. The needs of modern technology require a variety of well-understood high temperature processes creating protective oxide films.

Until recently there were many communications dealing with physics and chemistry of the surface separating the metal from the gas with the high temperature oxidation processes. Concepts of oxide film growth mechanisms were mainly based on the kinetics of the processes, which gives indirect information without real structural understanding. The initial oxide formation is a function of surface orientation, crystal defects at the surface, surface preparation and impurities in metal. Because of development of modern experimental methods for solid state surfaces, direct investigation and evaluation of theoretical ideas have accelerated the investigations in this field. Structural researches have been made by the transmission electron microscope, scanning electron microscope, Auger spectroscopy, X-ray crystallography, etc providing the progress of ideas about gas-solid interactions.

Although the peculiarities of the nucleation process of high temperature and low pressure of oxygen are quite well known, details of growth mechanisms are still not exactly determined or quantitative.

There are considerable gaps in the following areas:

- Obtaining direct evidence of the distinction between oxidation via lattice diffusion and oxidation via mutual diffusion of phases.
- Investigation of the operational function in connection with possible removal of molecules (atoms) from the surface into the volume of the solid body and the subsequent creation of a 3-D compound with the adsorbent.
- The influence of the surface preparation technology and impurities in the crystal on reactions taking place after chemisorption, leading to the growth of oxide films.

2. Techniques Available

Currently a modern research base is owned.

- Transmission electron microscopy with microdiffraction analyses.
- Diffraction of fast electrons by 'reflection' and by 'transmission' for the definition of phase composition and perfection of crystal surface.
- Definition of the main inner potential of the crystal lattice. This method is based on the reflection of fast electrons (original method, patented in the USSR).
- Computer simulation of the electron diffraction patterns of the single, twinned and two-phase crystals and the stereographic projections for any crystal systems (original software packages).
- Image analyses and fast Fourier transformation for obtaining the computer analogs of diffraction.
- Auger-spectrometry and mass-spectrometry of secondary ions for the definition of composition and profile of the element distribution.
- Scanning electron microscopy with an X-ray microanalyser.
- Ordinary, high temperature (1700°C) and quantitative optical metallography.
- X-ray diffraction method for the analyses of the diffuse scattering effects
- Measurements of the temperature spectrum of internal friction and shear modulus.
- Method of exoelectron emission (original device).
- Method for quick determination of corrosion resistance of metals and alloys (original device).
- Croygenic resistance measurements p(T,j,H) in the 10-300 K temperature range.

Besides, technologies have been worked out for chemical-thermal processing of fusions, thus increasing their heat-resistance. The group has also created fusions for high temperature exploitation in aggressive media, high temperature metal-ceramic knots for solid-oxide electrolytes. The results of the latter researches have not been published yet.

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Scientific Key Words: Alumina growth/breakdown; Aluminides; Ceramic coatings; Coating C/C composites; Computer modeling; Diffusion; Electrochemical measurements; Sensors; Silicides; Spallation; Sulfur segregation; Zirconia ceramics

Technical Key Words: Electrochemical microsensors; Energy plants; Engine applications

SCOPE OF RESEARCH

Fundamental Approach

The activities of the research group are mainly focused on transport of matter in oxide-based materials at high temperatures. The extension to fundamental aspects of high temperature oxidation of technical alloys and non-oxide ceramics is a logical consequence.

Applications

The applications comprise matter transport related projects in the following fields.

Specific Topics

1. Growth of Alumina Scales

Tracer diffusion and 'inert' marker studies, in conjunction with high resolution depth profiling (SIMS/SNMS) and computer simulation, have been used to identify growth mechanisms of such scales on various materials (e.g. FeCrAl, β-NiAl) with funding from national (German) agencies, or the European Union, via a BriteEuram project coordinated by the group and including French, British and other German partners.

2. Oxidation Protection of Non-Oxide Engineering Ceramics, Mainly SiC and Carbon-Reinforced Carbon (C/C)

Ternary oxide coatings are applied via Pulsed Laser Deposition (PLD) and electrophoreses, or combinations thereof. Their protectiveness in isothermal and cyclic oxidation experiments is investigated via thermogravimetry in combination with oxygen isotope diffusion studies (SIMS/SNMS) and model calculations. The work is funded by German national programmes.

3. Diffusion of the Constituent Elements in Doped Zirconia and Titanate Materials for SOFC and Oxygen Sensor Applications

Interfacial reactions, bulk transport, and grain boundary transport govern correct operation and degradation reactions, as well. Both aspects are studied using tracer diffusion and computer simulations. The work is funded via German national projects.

4. Diffusion in Intermetallics at High Temperatures

High temperature creep deformation and oxidation of intermetallic compounds may be controlled by diffusional transport. Therefore, diffusion of the constituent elements in silicides and aluminides is studied applying stable isotope tracers and radioisotopes in combination with sputtering techniques. The projects are funded by German national agencies.

Collaboration

Most of the projects are run either in the framework of a bilateral or multilateral partnership, both on a voluntary, or a formalized, basis as given, e.g., by a targeted programme funded by (mostly) national German agencies. The group is clearly interested to extend the scope of national and international coorporations if the expected synergy justifies the additional administrative and organisational loads on the partners.

Facilities

The main tool is SIMS/SNMS based surface analysis in combination with tracer diffusion. Standard thermogravimetry, Mossbauer spectroscopy and standard electron microscopy (SEM, TEM) as well as X-ray diffraction are available in the department.

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Scientific Key Words: Chemisorption; High-temperature water corrosion; Metal-metal oxide composite transport; Distribution; Chemical additives to water

Technical Key Words: Coal-fired boiler; Nuclear power systems; Steam generators; Steam turbine; Clean-up systems

SCOPE OF RESEARCH

Fundamental Research

One of the main topics of the research is optimizing of the chemical water conditions of larger water/steam-cycles, like steam generators or heating networks, on the basis of thermodynamic consideration, with special reference to cycles with more than one metal component. Further, the chemisorption including desorption of the hydrolyzable 3d-elements from aqueous solutions on to metal/metal oxide surfaces is being dealt with. This includes the investigation of the sorption dependence on temperature, pH, concentration and other water constituents.

In a recent development the group became concerned with the measurement of partition coefficients of several water constituents between the liquid and gaseous phases with the help of in-situ methods. This plays an important role on corrosion and corrosion protection.

Applications, Engineering Achievements and Technology Transfer

Specific Topics

1. Water Regimes of High-Temperature Cycles

This work is concentrated on the improvement of operational results of power stations and heating networks. A special aim is to optimize the transition processes between steady-state and transient operational conditions. Further, it is desired to clarify the best conditions for the use of bypass clean-up systems. The results are immediately incorporated by the power stations of VEAG Berlin and several heating stations.

2. Distribution of Water Constituents Between Solid and Liquid Phase

One special point is the minimizing of the activity build-up in nuclear power stations. Knowledge about the mechanism of this process, especially due to the chemisorption of 3d-elements, is now included in the investigation of desorption processes during the flooding of coal mines. This work is being carried out in collaboration with LMBV Berlin and with the Bundesministerium BMBF Bonn.

3. Distribution of Water Constituents Between Liquid and Gaseous Phase

This research is being carried out on the basis of the group's own financial resources. The group is trying to obtain a better understanding of the transition mechanisms of water constituents during the processes of vaporisation and first condensation, so that corrosion processes can be minimized.

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Technical Key Words: Engine materials; Aeroengines; Compressors; Diesel engines; Gas turbines; Land-based gas turbines; Thermal barrier coating systems

SCOPE OF RESEARCH

Fundamental Approach

The research is focused mainly on application of EB-PVD thermal barrier coatings (TBCs) on nickel-based superalloys for high-temperature use. Research covers coating processing, characterization and testing. The principal aim is to let turbine parts operate at higher temperatures and at an improved thermal efficiency. Major progress in this field is expected from zirconia based TBCs deposited on turbine vanes and blades by EB-PVD. The interplay between base material, bond coat and microstructurally designed TBCs under service-like conditions is investigated to particularly minimize oxidation and internal stresses between the single layers, thus preventing spallation of the TBC and improving the lifetime of the whole coating system. Testing includes isothermal and cyclic high-temperature exposure, thermomechanical testing as well as burner-rig testing. Furthermore, FEM calculations are in progress to model the stress situations in TBC systems.

Oxidation of conventional titanium alloys and titanium aluminides is being studied with respect to oxide scale formation and degradation of mechanical properties by interstitial solution of gaseous species in the subsurface zone. Intermetallic Ti-Al coatings have been developed to provide environmental protection especially paying regard to mechanical properties of the substrate material. Extensive mechanical tests were done to characterize the influence of the coating systems on tensile properties, creep and fatigue behavior of titanium alloys after long elevated temperature exposure and at high temperature, respectively. Recently, investigation of a new orthorhombic titanium aluminide alloy has been started. Furthermore, advanced aluminide coatings are being designed for optimized environmental protection as well as mechanical properties.

Applications, Engineering Achievements and Technology Transfer

Most work is devoted to the development of metallic and ceramic coating compositions and to their applicability on Ni base superalloys by the EB-PVD process. Cooperations exist with European manufacturers of aeroengine and stationary gas turbines and also with coatings and equipment producers. Supplementary experimental work is conducted by DC and RF sputtering of these compositions.

Specific Topics

1. Bond Coatings

Model bond coat compositions were developed which exhibit low oxidation rates, controlled interdiffusion and an intermediate coefficient of thermal expansion between superalloy matrix and zirconia top coat. Experiments address the applicability and performance of these layers under service conditions. They will allow prediction of the industrial processability of novel bond coat compositions by a multi-source EB-PVD process. Conventional MCrAlY coatings were compositionally (in a graded manner), or microstructurally, modified for comparative investigations on thermally activated alumina formation and thermocyclic/burner rig performance. Alumina scale growth on NiCoCrAlY coatings under various atmospheres was studied.

2. Thermal Barrier Coating Systems

The layer formation of various zirconia compositions on EB-PVD processing was studied and their performance under themocyclic loading was evaluated in order to understand their inherent potential for long-term heat protection. TBC adhesion and premature failure encountered in predeposition procedures (annealing environments, bead peening processing) was followed by thermocyclic and by TEM investigations. Besides predeposition procedures and compositional differences in the TBCs the microstructural design of the TBCs has a strong influence on their life. For the modification of the microstructure of the TBCs by variation of some important parameters like temperature and rotational speed of the substrate samples was systematically evaluated. Data for interfacial stresses and of E-modulus and Poisson's number are being generated for FEM calculations in cooperation with the materials science groups at the University of Karlsruhe and The Technical University of Berlin.

3. Hot Corrosion and Molten Salt Corrosion

Uncoated and coated nickel-based superalloys designed for use in gas turbine blades and vanes were tested under hot corrosion conditions in a high-velocity burner rig. The burner rig was also involved in a VAMAS (Versailles Project on Advanced Materials and Standards) programme that has aimed at the standardization of hot salt corrosion burner rig tests. For comparison with burner rig test results, an electrochemical method was used to simulate the sodium sulphate induced hot corrosion of uncoated and coated nickel-based superalloys. Current density versus potential curves were utilized for studying corrosive processes.

4. Oxidation and Protection of Titanium Alloys and Titanium Aluminides

The aim of this work is to get a fundamental understanding of failure mechanisms of uncoated and coated titanium based alloys and aluminides for use as compressor components in aeroengines. The influence of coatings on the mechanical properties of the base material is of great concern considering potential application as monolithic alloys as well as matrix material in titanium matrix composites (TMCs) at high temperatures. In this context, the effect of coatings on the fatigue properties of the base material is being carefully investigated.

Special Equipment

A dual source single beam EB-PVD equipment was installed. It offers production-like opportunities concerning evaporation rates and temperature regimes for the deposition of metallic and ceramic coatings on rotating substrates up to 400 mm long and 10 kg in weight. It is intended to process novel compositions of elements with widely varying vapor pressures and compositionally as well as microstructurally graded coatings.

For thermo-mechanical testing of internally air-cooled specimens a rig was designed at DLR to simulate service-like conditions for TBC systems particularly considering the radial temperature gradient.

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Technical Key Words: Waste incinerator materials; Furnace wall corrosion; Waste incineration; Waste pyrolysis; Ethylene pyrolysis; Steam reforming; Molten carbonate fuel cells; Thermal barrier coating systems; Syngas coolers; Hot gas cleanup; Petrochemical industry; Energy plants; Heat exchangers; Industrial furnaces

SCOPE OF RESEARCH

The research on high temperature corrosion at the MPI E in its beginning was mainly aimed at the elucidation of the mechanisms of attack on metals and alloys in more or less complex atmospheres. Starting with work on carburization in 1974, continuing with studies of oxidation-sulfidation, now oxidation-chloridation is the active topic. The reactions and processes in the formation of scales, mostly chromia scales, the ways of penetration by C, S, Cl, and of scale failure, were studied, but also the effects of these nonmetal and other ‘reactive’ elements on scale formation and protectivity. Recently a new main topic was added, 'metal dusting', a disintegration of metal materials upon carbon pickup (at $a_C > 1$). The mechanism of this corrosion process was elucidated, which is different for different alloys, but also ways and means for protection were developed. The latter aim became gradually of more importance and is also followed in the research on corrosion in environments simulating waste incineration conditions (flue gas with HCl and SO_2, deposits containing chlorides, sulfates etc.)

The emphasis of studies is on low and high alloy steels, forming magnetite, chromia or alumina scales. But also intermetallics were studied, especially NiAl and FeAl, while other laboratories in Germany concentrated on the Ti aluminides and some silicides.

The very good facilities for surface analytical studies (AES, SAM, XPS, LEED, SEM/STM, recently also SNMS) allow study of initial states of oxidation, processes at the oxide/metal interface and at grain boundaries in the oxide or alloy; these options are often used in planning and conducting the studies. However, the most general methods are thermogravimetry and discontinuous exposures, in atmospheres of any composition and below deposits.

The topics of research are conceived and chosen by the principal investigator, independently. However, they are chosen so that the research is of fundamental interest and also relevant for application - the projects should lead to progress in understanding of high temperature corrosion phenomena but also lead to ways and means to avoid corrosion or to develop materials with improved corrosion resistance. All research projects need funding, which comes from institutions, such as Deutsche Forschungsgemeinschaft, Bundesminister für Bildung und Forschung, and the European Community for Coal and Steel, but also from some industrial companies.

Specific Topics

1. Metal Dusting, Mechanisms and Ways of Protection

In strongly carburizing atmospheres ($a_C > 1$) a disintegration of metallic materials can occur under formation of a dust of metal particles, carbon (graphite) and sometimes oxides and carbides. In recent years, many failure cases were observed in atmospheres obtained by reforming natural gas and used for synthesis, reduction of iron ores etc., but also in other chemical and petrochemical processes. The different mechanisms of metal dusting for iron and low alloy steels, for high alloy steels and for Ni-base alloys have been elucidated in the recent years, in collaboration with a group at the Max-Planck-Institut für Mikrostrukturforschung (Woltersdorf, J., Pippel, E., Schneider, R.) which did TEM studies supplementary to the broad approach at the MPI E. One way of protection is by a protective oxide scale, i.e. usually a spinel/chromia scale in the most critical temperature range (around 600°C). Ways and means to obtain a protective scale are studied on ferritic and austenitic steels; very important is the surface state, and microstructure - a fine grained structure and surface-near deformation provide fast diffusion paths for supply of Cr to the surface for scale formation. The role of alloying elements in high alloy steels (Alloy 800) is studied in detail.

The other way of protection is by poisoning the surface for carbon ingress and for the start of metal dusting, which is possible by sulfur and some other means. Quantitative studies of such effects were firstly done at the MPI E. The presence of sulfur, e.g. adsorbed from H_2S, stabilizes cementite Fe_3C on iron, otherwise the cementite decomposes, which is the metal dusting mechanism for iron. This stabilization is used now in a fundamental study of Fe_3C concerning thermodynamics, nonstoichiometry, diffusivities etc.

Many studies, e.g. on failure cases, long-term plant and laboratory exposures, have been conducted, partially supported by metal producers, petrochemical and chemical-engineering companies, and a vast experience and knowledge has been compiled on the ranking of alloys concerning metal dusting resistance and on their different metal dusting behavior.

2. Development of High Temperature Corrosion Resistant Materials for Aggressive Environments

At present for the heat exchangers in waste incineration plants, mainly low alloy steels are used which, due to corrosion by HCl and SO_2 in the atmosphere and by chlorides and sulfates in the deposits, generally last up to 1-2 years. In previous studies, the mechanisms of the complex chemical and corrosion processes in the system atmosphere/deposits/scale/metal phase have been elucidated. Most dangerous is the 'active oxidation', an accelerated formation of non-protective scales, catalyzed by chlorine, which stems from HCl or chlorides in the deposits. An important and surprising result was the positive effect of SO_2, reducing attack by active corrosion, since in the presence of SO_2 the chlorides in the deposits are mostly converted to sulfates which are less dangerous than chlorides in the temperature range of interest, 300-500°C. But, development of more corrosion-resistant materials is necessary and two ways are being studied:

(i) For the coating of heat exchanger tubes, ferritic alloys containing high concentrations of Cr and Si, are tested under waste incineration conditions. These alloys proved to be more corrosion resistant than any other high-alloy bulk materials and coatings. Research and development now concentrate on coating by high velocity thermal spraying.

(ii) The improvement of stainless steels on the base of Fe-18Cr-10Ni to attain fast formation of a protective spinel/chromia scale. The alloy composition will be varied but also the microstructure. A stabilized fine-grain structure and also an appropriate surface finish method is expected to lead to fast diffusion paths for Cr and rapid scale formation.

The first development (i) is in cooperation with German industry and institutions, working on the coating technology. The second project (ii) involves French, Spanish, and Swedish steel companies and is funded by the ECSC. This project certainly also can lead to `metal dusting' resistant steels.

A very special task is the development of materials for molten carbonate fuel cells, which must be resistant against carbonate metals at 650°C and on the other hand sustain a sufficient electrical conductivity, for use as current collectors. Therefore, formation of the usual protective oxide scales, chromia or alumina, which are insulating would be disadvantageous. The scales aimed at are mixed spinels of various alloying elements, warranting sufficient conductivity and good protection. The scale compositions and formulation mechanisms were elucidated for various austenitic steels and model alloys. Steels with relatively low Cr-content, but considerable concentrations of Ni, Co, and Mn, could be recommended for the application in the molten carbonate fuel cells.

3. *Oxidation of Intermetallics*

After extended research on NiAl oxidation, now for comparison FeAl is studied. These aluminides show some interesting common features: (i) In the temperature range 750-1050°C at first metastable γ- and θ-Al_2O_3 are formed and afterwards replaced by α-Al_2O_3, which is favored with increasing temperature and certain alloying additions (Cr, Y). (ii) Voids and cavities are formed by Al-depletion and Ni(Fe) inward diffusion beneath the oxide scale, and probably also at grain boundaries. (iii) The latter effect leads to intergranular oxidation of NiAl. But, also (iv) internal oxidation of NiAl is observed under certain conditions.

After some summarizing publications and actions in 1996, e.g. the European workshop on Oxidation of Intermetallics, the interest in this topic fades away, at least at the MPI E.

4. *Effects of `Active Elements' in the Nucleation and Growth of Chromia and Alumina Scales*

This topic includes the so-called rare-earth element effects but also effects of nonmetal elements, such as S, N, C, Cl and P. Using the good facilities for surface analytical (AES, XPS) and surface-structural studies (LEED, SEM, XRD), a joint approach is possible with kinetic studies. For example, it could be clearly shown that Y already plays a role in the nucleation of Al-oxide on Fe-Cr-Al alloys. The effects of the presence of S, N or C on the formation of Cr_2O_3 on Fe-Cr and Ni-Cr alloys were elucidated. A great help in such studies is the knowledge collected at the MPI E on two-dimensional surface compounds, such as ‘CrN’ or ‘CrC’, which can form as intermediates in oxidation processes in the presence of nitrogen or carbon. The study of the thermodynamics and structures of such surface compounds has been an important topic in the MPI E since about 10 years.

5. Guidelines and Standards in High Temperature Corrosion Research and Testing

There are only very few standards on high temperature corrosion testing and a general lack of guidelines and agreements on how to conduct experiments and tests and how to avoid errors and mistakes. In an European workshop in June 1994, the methods and techniques were put forward based on the experience of many researchers - discussed and later on recommendations were published in a book: ‘Guidelines on Methods and Testing in High Temperature Corrosion Research’. Further steps have been taken in the development of best practices and standards, in which the MPI E is strongly involved:

(i) A European project on ‘Discontinuous corrosion testing in high temperature atmospheres’, with the partners: ERA, NPL, Cranfield University, MPI E, Krupp VDM, JRC Petten, Sandvik, Avesta Sheffield, SIMR, ENEL-CRAM, in which the group takes the main responsibility concerning reference experiments and definition of gas atmospheres, and

(ii) A project ‘Best Practice for the Carburization Testing of Alloys’ for the initiation of standards in "Discontinuous Gas Carburization of Alloys" and "Pack Carburization of Alloys for Steam-Cracking Tubes" sponsored by Mat. Technology Institute St. Louis (concluded).

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Scientific Key Words: Bond/thermal barrier coatings; Superalloys; Aluminides; Silicides; High temperature X-ray diffraction; in-situ studies

Technical Key Words: Gas turbines; Thermal barrier coating systems; Energy plants; Supercritical water oxidation (SCWO)

SCOPE OF RESEARCH

The activities on the topic of high temperature corrosion at the Fraunhofer-Institut für Chemische Technologie consist of research works closely related with application in practice and special topics in innovation and fundamental research. Fundamental developments are introduced immediately into applied research, which is carried out in direct cooperation with the customers.

Experimental Methods

The experimental work emphasizes the use of high temperature X-ray diffractometry as an in-situ method, with post oxidation studies by interference microscopy and the electron microprobe.

The time and temperature resolved X-ray diffraction is an effective in-situ method for studies of high temperature corrosion. The measuring system consists of an X-ray diffractometer with a high temperature device recording series of diffraction patterns, showing the changes in the sample as a function of time or temperature. The method yields the following information in-situ:

- Identification of the corrosion products and their modifications.
- Kinetic evaluation for the formation of each corrosion product individually.

- Thermal dilatation of all phases in the oxide scale and in the substrate simultaneously.
- Texture changes and formation of stresses.

After the in-situ experiments the samples are investigated by electron microprobe or interference microscopy leading to a complete information about the oxide scale formation.

Current and Recent Research Work

The research work in the last years has been focused mainly on topics related to gas turbines for electric power generation and on special questions relating to the oxidation behaviour of several intermetallics. The turbine blade aspects are closely related to application; meanwhile fundamental research is carried out on the oxidation of intermetallic phases.

Specific Topics

1. Turbine Blade Materials

The oxidation behaviour of superalloys for application in gas turbine blades is studied in the relevant temperature ranges using the high temperature X-ray diffraction. The scope of the research is to obtain in-situ information about the influence of the Al and Cr contents on the formation of protective alumina scales and about the formation of other, eventually transient oxidation products. The formed oxides are identified in-situ and their formation is monitored as a function of time simultaneously for each oxidation product. Post oxidation studies by means of electron microprobe are performed in order to complete the information about the oxidation behaviour.

2. MCrAlY Coatings for Turbine Blades

The oxidation resistance of the MCrAlY coatings (M=Ni/Co) controls mainly the lifetime of the blades in modern stationary gas turbines for electric power generation. Improving the oxidation resistance of the coating allows increase of the working temperature of the turbine, providing a higher efficiency. The objective of the research work is to study the influence of the coating composition and of the temperature on the oxidation behaviour and phase stability. Studies of the oxidation in the initial state by means of the in-situ X-ray diffraction are carried out, as well as long-term experiments for life time prediction.

3. Intermetallic Phases

The high temperature oxidation of the intermetallic phases NiAl, FeAl, TiAl, $MoSi_2$ and $TiSi_2$ has been studied using the in-situ X-ray diffraction. In the case of the aluminides the emphasis is placed on the influence of the temperature, dopant elements and aluminum content on the formation of metastable alumina phases. The studies of the disilicides has been focussed on the influence of the temperature on the SiO_2 modification.

4. Thermal Barrier Coatings

The phase stability of partial stabilized zirconia has been studied in-situ by means of high temperature X-ray diffraction. Deviations in the dilatation behaviour and reversible and irreversible changes in the phase composition have been observed. The scope of the research work is to obtain additional information contributing to a better understanding of the thermal barrier coating system.

5. Corrosion under the Conditions of Supercritical Water Oxidation (SCWO)

The Supercritical Water Oxidation (SCWO) is an efficient procedure for converting hazardous residues into environmentally friendly products. The reactor material, however, is subjected to a highly corrosive medium and to high pressures and high temperatures. An experimental set-up was designed that allows corrosion studies under these conditions. A series of materials like Ni-base alloys IN625, IN686 and Alloy 59 has been studied at 500°C and 46.5 Mpa up to 300 h with a model fluid consisting of $HCl+H_2O+NaCl$ using H_2O_2 as oxidant.

Future Plans

A continuous development of the experimental possibilities and evaluation procedures, such as further reaction models for a quantitative kinetic evaluation of the corrosion reactions observed in-situ by X-ray diffraction, is an important part of the research works. The experimental emphasis on the combination of high temperature X-ray diffraction as an in-situ method and post oxidation studies by electron microprobe will play a central role offering a complete characterization and understanding of the studied systems and reactions. The research works will be concentrated further on topics related to gas turbines and special aspects of fundamental research. The group, however, is open to any new input due to new interests and requirements.

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Scientific Key Words: Ceramics corrosion; Ceramics oxidation; Hot corrosion; Thermodynamic modeling; Life prediction; Non-oxide ceramics

Technical Key Words: Engine materials; Gas turbines; Ceramic components; Ceramic filter durability; Automotive engines

SCOPE OF RESEARCH

Fundamental Approach

The oxidation and corrosion of non-oxide ceramics, in particular Si_3N_4 and SiC-based materials, is the main thrust of research. The aim is to bring together thermodynamic calculations, kinetic modeling and mechanical property measurement (4-point-bending to 1400°C) to allow life time predictions. The conditions range from hot corrosion (e.g. by Na_2SO_4, Na_2CO_3, T = 700-1300°C) and hydrothermal corrosion (P to 2 kbar, T = 100-800°C) to oxidation and corrosion to 1700°C. Atmospheres: air, O_2, N_2, Ar, CO_x, mixtures. Microstructural development is also an important parameter investigated. Thus phase relations, e.g. in the Y-Si-O-N system, are investigated. Kinetic modeling of oxidation and corrosion processes is performed.

Applications, Engineering Achievements and Technology Transfer

Fundamental studies are directed to high-temperature limits of advanced ceramics and the application of corrosion to make new products (carbon layers, see below). Industrial applications are gas turbine components, soot filtering devices, engine components such as valves. Projects are sponsored either by DFG, EU or industrial partners. Examples are given in the following abstracts:

Specific Topics

1. Fundamental Research into Phase Relations and Corrosion

Simple system studies (Si-O-N, Y-Si-O-N) are directed towards the absolute limits of use for nitrides and carbides, often defined by "secondary active-passive boundaries", e.g. the ambient pressure is exceeded by gaseous corrosion products, leading to bubbling and spallation. Sponsorship is by DFG.

2. Structure of Oxidation Scales on SiC and Si_3N_4

Fundamental research into the scale development, with special interest in crystallisation of phases from amorphous products, is undertaken. Ways to influence this behavior are explored (atmosphere control, H_2O, surface modification) to gain improved life-time and its prediction. Collaboration takes place with CNRS (F), laboratories of, or derived from, the Academy of Sciences in Kiew (IPMS, MRC) and Minsk (ISSPS), ESK Ltd, ABB. Sponsorship is by EU (Inco-Copernicus).

3. Carbon Production by Hydrothermal Treatments

A new way for the production of carbon (layers, powder) is being investigated. Hydrothermal corrosion of carbide leaves C, ranging in structure from graphitic to amorphous or diamond-like is being studied. Layers from nm to microns in size can be made. Possible applications are catalytic coatings, or layers for wear resistance or chemical resistance on parts or fibres. Sponsorship is by DFG.

4. SiC as Soot Filtering Material

The chemical stability of SiC in soot filtering was investigated in regeneration related environments (C-H-O-atmospheres, hot corrosion conditions). The work is sponsored by JRC of automotive companies (Volvo, DB, VW, Fiat, Renault, Rover).

5. Corrosion of Si_3N_4 for Valve Applications

The influence of (mainly hot corroding) agents on valve materials from Si_3N_4 is investigated. Fundamental mechanisms, implications for mechanical properties and reliability are explored. The research is sponsored by Daimler-Benz AG.

Special Equipment

Thermal Analysis to 1700°C.
Micro-Raman-Spectroscopy
Hydrothermal Laboratory (to 1000°C, 5 kb).

Networks

There is a Working Group, "Corrosion of Ceramic Materials" under the German Ceramic Soc. (DKG) and the German Materials Soc. (DGM), with approximately 30 active members from universities, research centers and industry. Two meetings are held per year and Prof. Nickel is the chairman.

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Scientific Key Words: Alumina; Mathematical modeling; Mechanical testing; Nodular growth; Stress measurement; Optical fluorescence spectroscopy

Technical Key Words: Thermal barrier coating systems

SCOPE OF RESEARCH

Fundamental Approach

The research is devoted to the analysis of the morphological development of oxide scales and the relationship between the scale morphology and the protective properties of the scales. Theoretical investigations include the modeling of diffusion-reaction processes during scale growth. Special problems of interest are the development of a rough oxide-metal interface owing to a diffusion-controlled morphological instability, and the formation of interfacial pores which are detrimental to the scale adherence. Experimental investigations concern the analysis of the fracture behavior of oxide scales. In particular, stresses in α-alumina scales at room temperature were determined with high spatial resolution by using optical fluorescence spectroscopy. Scale failure has mainly been studied under a graded scale loading induced by an appropriate substrate deformation. The aim of this approach is to determine fracture-mechanical properties of oxide scales by an ex-situ analysis of crack and delamination patterns of the scales. The investigations were financially supported by the Deutsche Forschungsgemeinschaft (Germany).

Applications, Engineering Achievements and Technology Transfer

The analysis of the mechanical properties of oxide scales is of great practical relevance. The bend and indentation tests used in the present studies for elucidating the failure mechanisms of scales are relatively easily to perform also at high temperatures.

Indentation experiments, as only weakly destructive tests, seem to be suited for comparative studies of scale cracking and delamination. The establishment of a graded scale loading, e. g. by an appropriate bending of samples, could provide an effective ex-situ analysis of the fracture behavior of oxide scales. A beneficial aspect of the technique of optical fluorescence spectroscopy is the possibility to analyze stresses in buried
α-alumina scales provided the covering layer is sufficiently transparent. Thus, stresses could be examined, for example, in the alumina scale growing in thermal barrier coatings at the interface between zirconia and the bond layer when α-alumina is formed at sufficiently high temperatures.

Specific Topics

1. Modeling of Diffusion-Reaction Processes During Scale Growth

The aim of the modeling of diffusion-reaction processes during oxidation is the quantitative understanding of the scale growth. This work includes one-dimensional simulations of the out-diffusion of the less noble metal during the selective oxidation of binary alloys, as well as two-dimensional simulations of the unstable roughening of the oxide-metal interface based on finite difference methods. The theoretical investigations were performed in close co-operation with experimental studies of the scale growth on Ni_3Al and NiAl by Rühle, M., Prof., and Schumann, E., Dr., (Max-Planck-Institute, Stuttgart). For example, the theoretical analysis showed that the growth of oxide intrusions into the metal during the initial oxidation of Ni_3Al at low oxygen partial pressure could be affected by a morphological instability of the oxide-metal interface due to a relatively fast initial inward diffusion of oxygen through the scale. From measurements of the Al-depletion profile after oxidation of NiAl at the Max-Planck-Institute in Stuttgart, the interdiffusion coefficient of NiAl was calculated by means of a modified Boltzmann-Matano analysis.

2. Stress Measurement and Fracture Behavior of Scales

The analysis of the fracture behavior of α-alumina scales includes the measurement of mechanical stresses in the scale at room temperature by means of optical fluorescence spectroscopy. These measurements are carried out in close co-operation with Clarke, D.R., Prof., and coworkers (University of California Santa Barbara). Optical fluorescence spectroscopy was firstly applied to measure stresses in thin alumina scales by Clarke and Lipkin in 1993. Similar to Raman spectroscopy, this method permits a high spatial resolution of the stress measurement in the 1μm-region. It yields, however, only the trace of the stress tensor for polycrystalline alumina. A local stress analysis in scales on NiAl suggested the presence of large spatial stress fluctuations which are presumably connected with the high roughness of the scale due to the appearance of oxide ridges. Current investigations concern the proper interpretation of spectroscopic data in terms of stresses. Problems arise when both the stress state and the Cr concentration in the probed volume are non-uniform since the fluorescence signal is proportional to the Cr concentration in α-alumina.

The failure mechanisms and fracture-mechanical properties of alumina scales on NiAl and FeCrAl were investigated by bend and indentation tests at room and oxidation temperature.

The analysis of crack and spallation patterns occurred ex-situ at room temperature. The graded loading of the scale on the side face of bending bars after four-point bending allows in principal to estimate lower bounds of the fracture strain and strength of the oxide from the observed damage patterns. Furthermore, the lateral propagation of through-thickness scale cracks is sensitive to the fracture toughness of the oxide.

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Scientific Key Words: Life prediction; Thermal cycling; Surface analytical methods; Oxidation diagrams; Mathematical modeling

Technical Key Words: Gas turbines; Lifetime prediction; Creep/corrosion interactions; Mixed oxidants with water vapor; Thermal barrier coating systems

SCOPE OF RESEARCH

Fundamental Approach

The aim of the research is to investigate the behavior of materials in aggressive environments at high temperatures. Special emphasis is placed on the formation, growth, adherence and long-term integrity of the protective surface oxide scales.

The studies include investigations of the scale-growth mechanisms as well as the long-term behavior (experiments up to 10 000 h) under actual service conditions. The experimental conditions are mainly related to the materials behavior in energy conversion systems such as gas turbines, combustion and gasification plants as well as waste incineration systems. The long-term aim is to incorporate the results of the fundamental research into the technologically oriented studies to develop models which enable prediction of long-term component behavior under actual service conditions. In the experimental and modeling work both corrosion, as well as the interaction between corrosion and mechanical properties (mainly creep), are addressed.

Applications, Engineering Achievements and Technology Transfer

Next to fundamental studies on oxide scale growth and adherence, extensive studies are being carried out concerning the long-term material behaviour under realistic service conditions. Most of the latter studies are either directly funded by industry within bilateral contracts, or carried out in cooperation with industry, e.g. with common government or EU funding.

Specific Topics

1. Mechanisms of Oxide Scale Growth and Adherence

Growth processes of chromia and alumina scales on high-temperature alloys at high and low oxygen partial pressures are being investigated by two-stage oxidation using ^{18}O and $H_2{}^{18}O$-tracers. The surface scales formed during this oxidation process at temperatures in the range 600-1200°C are studied by a number of analytical techniques, such as SIMS, SNMS, RBS, SEM/EDX, EPMA and TEM. Mathematical models are being developed to describe diffusion processes in the scale, as well as depletion phenomena in the sub-surface depletion zone.

Fundamental aspects of oxide scale adherence are being investigated using a number of experimental methods, such as the scratch test and acoustic emission analysis, in combination with various surface analytical techniques such as AES and RBS. Stresses in oxide scales, determined using X-ray diffraction and LRS, are correlated with scale adherence measured under thermal cycling conditions.

2. Intermetallics

A small project is being carried out concerning intermetallics on the basis of γ-TiAl, mainly for applications in gas turbines. The studies include fundamental aspects of scale formation as well as determination of long-term materials behavior. The present programme is mainly aimed at the development of alloys which form protective alumina scales upon long time exposure.

3. Solid Oxide Fuel Cells

The behavior of the metallic interconnector of solid-oxide fuel cells (SOFC's) is being studied in oxidizing and reducing environments in the temperature range 700-1000°C. Depending on the actual fuel cell operation temperature, two types of alloys are presently investigated: ferritic steels and Cr-based ODS alloys. The studies concentrate on the actual corrosion behavior of the metallic materials in the SOFC environments, but also on the interaction of the metals with the perovskite type ceramic electrode or contact materials. In relation to the latter subject, major efforts are being put into the measurement of high temperature electrical conductivity of metal/ceramic bonds, as well as the development of protection methods against cell degradation by volatile chromium oxides and oxy-hydroxides.

4. Corrosion and Corrosion/Creep Interaction of Materials for Heat Exchangers in Advanced Power Plants

The effect of carbon-, sulfur- and/or chlorine-bearing gas species in oxidizing environments on the behavior of metallic materials is being studied. The main emphasis is being placed on the development of mathematical models predicting various modes of corrosion attack as a function of alloy composition and environmental conditions. The present program is strongly connected with the development of new materials for heat exchanging components in power plants with advanced steam conditions. In this context, increasing efforts are being put into studies on steam oxidation of new ferritic and austenitic steels, as well as Ni-based alloys for heat exchangers and steam turbine components.

5. TBC/MCrAlY-Coating Systems

For turbine components subjected to very high gas temperatures, TBC coatings are being developed. The program mainly addresses the effect of MCrAlY-based coat oxidation performance on TBC coating life. In co-operation with industry new MCrAlY-coating types are being developed. The MCrAlY and TBC coatings are being applied by plasma spraying and tested during isothermal as well as cyclic oxidation. Significant efforts are being put into the development of analytical methods such as imaging-SNMS for the characterisation of the MCrAlY/TBC interface.

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Scientific Key Words: Alumina growth; Intermetallics; Interfaces; Reactive element effect; Transmission electron microscopy

SCOPE OF RESEARCH

Fundamental Approach

The main interest is in fundamental research on high temperature oxidation. The focus thereby is on the microstructural development of protective scales during oxidation of alloys and intermetallics. The studies are performed using the whole spectrum of modern electron microscopy techniques, including high-resolution (HREM) and analytical transmission electron microscopy (e.g. STEM). Problems which are being studied are the reactive element effect, e.g. the influence of dopants (Y, Ti) or impurities (S) on the oxidation of alumina-formers (NiAl, FeCrAl). The segregation of reactive elements at scale grain boundaries and the metal/scale interface is also studied. Another project is on the oxidation of TiAl, which under practical conditions does not form protective alumina scales. Analytical studies have been conducted in order to identify the mechanism by which nitrogen prevents the formation of a protective oxide. The results highlight the critical role of the composition of the metal/scale interface for the corrosion process.

Recently the focus of the research has been broadened. Mechanical stresses in alumina scales have been determined using a new optical fluorescence method. This method allows the measurement of residual stresses with high spatial resolution, which is important in order to understand scale spallation and stress relaxation mechanisms.

Cooperation with other groups has been established, for example with the group of Meier, G.H., Professor and Pettit, F.S., Professor, at the University of Pittsburgh, with Grabke, H.J., Professor, from the Max-Planck-Institut für Eisenforschung in Düsseldorf as well as with Graham, M.J., Professor, from the National Research Council of Canada in Ottawa.

Sponsors, are indicated in the following abstracts.

Specific Topics

1. Oxidation of Intermetallics

This research is being carried out in collaboration with Pompe, W., Professor, Max-Planck-Group Dresden, as part of the high temperature corrosion research program of the Deutsche Forschungsgemeinschaft. The aim is the analysis and modelling of scales formed on intermetallics (NiAl, TiAl). The work on NiAl includes microstructural and mechanical characterization. The composition of scales and subscale metal developed during oxidation of TiAl are studied using analytical TEM and advanced electron diffraction methods.

2. The Adhesion of Oxide Scales on FeCrAl Alloys

This research is carried out together with other researchers from universities and industries in Europe, with the overall goal to improve the adhesion of oxide scales formed on FeCrAl alloys. This project is sponsored by the Commission of the European Union as part of the EURAM/BRITE program. Model alloys with different compositions have been produced, which are compared with state-of-the-art commercial alloys. The work in Stuttgart includes the characterization of alloys and scales as well as the measurement of internal stresses in alumina.

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Scientific Key Words: Acoustic emission; Chloridation; Coated and uncoated super alloys; Corrosion-mechanical properties interactions; Cyclic oxidation; Heat-resistant steels; Interfacial effects; Intermetallics; Sulfidation

Technical Key Words: Coal gasification; Combined cycle system; Aeroengines; Gas turbines; Energy plants

SCOPE OF RESEARCH

Fundamental Approach

The work focuses on the limits of the protective effect of surface scales (oxides, sulfides, scales on protective coatings, etc.) in different atmospheres, with and without superimposed mechanical or thermocyclic loading. The main aim is the understanding and the modeling of the damage mechanisms leading to scale fracture, loss of scale adhesion and breakaway effects in oxidation. Another aim is to throw light on the growth mechanisms of the scales with respect to their role for long-term protective behavior. The investigations are carried out in air and more aggressive atmospheres e.g. H_2S-, Cl_2- and HCl-containing atmospheres. Many of the tests are accompanied by acoustic emission measurements in order to detect scale damage. The materials covered are low and high alloy steels, Ni-base alloys, TiAl-alloys and silicides.

Applications, Engineering Achievements and Technology Transfer

Most of the work is in undertaking fundamental studies under near-service conditions in order to develop recommendations for materials use and development. A new type of coating has been developed for protection in H_2S atmospheres and the 'chlorine effect' has been developed as a surface treatment for significantly improving the oxidation resistance of TiAl-materials. Many of the projects are undertaken with consortia of industrial partners, thus, promoting technology transfer.

Specific Topics

1. Oxidation of Molybdenum and Titanium Disilicide

This project is carried out in collaboration with Cesiwid, H.C. Starck and Technical University of Aachen under the sponsorship of the German Materials Research program. The aim of the work is to develop recommendations for the improvement of silicide materials for the use in aggressive combustion atmospheres. The corrosion tests and the microstructural evaluation as well as the modeling of the corrosion processes are performed at KWI.

2. Oxidation of TiAl-Alloys

Projects are running on the initial stages of TiAl-oxidation, funded by Deutsche Forschungsgemeinschaft, and on the oxidation behavior of P/M-TiAl-alloys, funded by the German Materials Research Program. In the first case the oxidation products after several minutes up to 100 hrs are characterized by TEM investigations and correlated with oxidation kinetics. In the second case several P/M-versions are tested concerning their oxidation resistance. This project is carried out in collaboration with Metallgesellschaft, MTU, BMW-Rolls Royce, FIA and GfE. A surprising improvement of oxidation resistance has been achieved by using the ‘chlorine effect’.

3. The Influence of Water Vapor on the High Temperature Mechanical Properties of TiAl-Alloys

The project is funded by the German Ministry of Economy and performed in cooperation with MTU, Tital, ABB and Siemens. Creep strength can be significantly affected by the presence of water vapor and the investigations also include the water vapor effect on fatigue behavior.

4. The Influence of HCl-Impurities in Combustion Atmospheres on the Oxidation of Advanced Ni-Base Alloys and Coatings

This work is carried out in collaboration with Siemens, ABB and MTU and funded by the German Ministry of Economy. Small amounts of HCl impurities may decrease adhesion of protective oxide scales so that internal corrosion is increased due to the loss of the protective effect under thermal cycling and under mechanical load. In the test near-service conditions of simultaneous load and temperature changes are applied and it turns out that optimizing the Y-content in particular in coatings can overcome the detrimental effects of HCl impurities.

5. Improvement of the Resistance Against H_2S-High-Temperature Corrosion by Coatings

Funded by the German Ministry of Economy, and supported by a committee of companies including MAN-GHH, Siemens, Ciba-Geigy, Lab and Bayer, several potential new protective coatings based on aluminides and silicides are investigated in this project. Good protection is achieved up to 700°C for a TiAl-type coating.

6. Materials for the Use in Cl-containing High Temperature Environments

The project funded by the German Ministry of Economy and supported by VDM and Robert Zapp, aims at identifying the role of simultaneous mechanical stresses and chlorine attack for several commercial Ni-base alloys. The damage mechanisms are identified and modeled, and a life-time prediction procedure is developed for these conditions.

7. Development of a Test Procedure Characterizing Corrosion Resistance at Temperatures above 1500°C

This work is part of the COST 510 action and performed in collaboration with Cesiwid, Carbolite and the Universities of Erlangen and Vienna. A special thermogravimetric equipment has been developed together with Carbolite allowing the separation of negative effects by equipment oxidation from the thermogravimetric results of the specimen. Several exotic ceramics partially supplied as most recent developments from Russian ceramics research are being tested.

8. The Role of Cr-Depletion in the Metal Subsurface for the Oxidation Behavior of 9 Cr Steels With and Without Superimposed Mechanical Load at 650°C

The project is part of the European Human Capital and Mobility Action, performed together with 9 labs in other European countries. A significant drop in oxidation resistance due to Cr-depletion during oxidation is found for X20 CrMo 12 1 with about 10.4 Cr and for Nf 616. Small additions of Si seem to improve the oxidation resistance of 9 Cr-steels. Creep deformation enhances the local formation of Fe-rich non-protective oxides.

9. Adhesion Strength of Oxide Scales

Adhesion of oxide scales on TiAl and on pure Ni is measured in a modified 4 point-bending test, accompanied by acoustic emission measurements at temperatures up to 900°C. The project is funded by the Deutsche Forschungsgemeinschaft.

10. Measurement of Growth Stresses in Oxide Scales

In this project the unilateral strip oxidation test has been modified with a continuous electronic measurement system which records bending as a function of oxidation time. At present the growth stresses are measured for the oxide scales on TiAl and on pure Ni. Further scale/metal systems will follow. Critical growth stress levels for microcracking in the scales are detected by acoustic emission. The project is funded by the Deutsche Forschungsgemeinschaft.

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Scientific Key Words: Interface structure; Metal-oxide formation; Aluminides; Silicides; Thermal cycling; Chemical vapor deposition; Surface analytical methods

SCOPE OF RESEARCH

Fundamental Approach

The aim of the research is to understand the formation and growth behavior of corrosive layers which are formed by oxidation, hydrogenation, sulfidation, chloridation, nitridation, carbonation and silicide formation on a microscopic level. The group therefore combines classical methods like thermogravimetry, volumetry and resistometry with surface analytical tools like electron spectroscopic techniques (AES, XPS, UPS), diffraction methods (LEED) and scanning probe microscopy (STM, AFM) in order to characterize the initial steps during the formation of the scales and to understand the underlying kinetic and thermodynamic processes. It is believed that this approach leads to a better understanding of the phase boundary region between metals or alloys and the corrosive layer. The work which is introduced in the following abstracts is financed by the Deutsche Forschungsgemeinschaft (DFG).

Specific Topics

1. High-Temperature Corrosion of Nickel-Aluminides in Complex Gas Mixtures

The kinetics of high temperature corrosion of nickel-aluminides was measured gravimetrically. The resulting morphology of the corrosion products was analyzed with light and electron microscopy, whereas the elemental composition of the corrosive layers was elucidated from Auger microprobe analysis. A mixture of H_2 and HCl resulted in an almost selective chloridation of Al. The speed of the chloridation increased with the aluminum content of the sample, with the rate-determining step being the transport of the aluminum chlorides in the gas phase through the pores in the scale. The sulfidation in a H_2-H_2S gas mixture showed a parabolic time dependence, but was almost independent of the aluminum content in the range of 25 to 45% Al. The result of the reaction is a multilayer system (Ni_3S_2 outside and $NiAl_{3.5}S_{5.5}$ inside) which is independent of the H_2S partial pressure (1 - 10 vol%.) in the temperature range from 750°C to 950°C. The growth of the sulfide is accomplished by diffusion of nickel cations to the surface and of sulfide anions into the bulk. Reaction of NiAl with an aluminum content of less than 25% resulted in a layer with low Al content and inner sulfidation of aluminum. Low oxygen partial pressures in the H_2-H_2O-H_2S system suppressed the sulfidation but the inner oxidation was enhanced, which resulted in the destruction of the metallic samples within a rather short time.

2. Oxidation Mechanism of Titanium Aluminides

The formation of a protective Al_2O_3 layer depends on the Al content of the titanium aluminides, on their structure, the previous surface treatment, the reaction temperature and the purity of the oxygen. An atmosphere of pure oxygen resulted in the selective oxidation of Ti55Al and the formation of an Al_2O_3 layer. The corrosive multilayer consisted of an outer TiO_2 scale, followed by an Al_2O_3-rich layer. A mixture of TiO_2 and Al_2O_3 is formed at low aluminum contents. This complex multilayer system showed only little lateral expansion which increased with decreasing aluminum content. A N_2-O_2 gas mixture suppressed the formation of the protecting Al_2O_3 surface layer almost completely, but the above mentioned complex multilayer system could also be found. Segregation of TiN is observed at the boundary layer between the oxide and the titanium aluminide. Titanium aluminides with an Al content between 45 and 55%, which were oxidized in a H_2-H_2O gas mixture, showed a large region with decreased Al content underneath the complex multilayer oxide. It consists of segregated Al_2O_3 and a homogenous a_2-Ti_3Al phase.

3. The Influence of the Surrounding Environment on the Threshold of Corrosion Fatigue

The influence of dry hydrogen, oxygen and water vapor on the threshold of corrosion fatigue of the 90MnV8 steel has been studied. The aim was to elucidate the parameters for the formation of cracks in the samples. The influence of the gas mixture on the threshold microstructure was analyzed by REM and TEM.

4. Study of the Initial Steps during High Temperature Oxidation of Metallic Materials by in-situ UHV-STM

The initial steps during high-temperature oxidation of clean metal surfaces will be investigated with respect to oxide nucleation and growth with in-situ STM. The aim will be the structural characterization of the interface during isothermal experimental conditions. The group will also try to correlate the oxide nucleation and growth behavior with the crystallographic orientation of the substrate. Additionally, the influence of thermal cycling will be investigated, with special emphasis on the thermal expansion and the subsequent misfit between the metallic substrate and the oxide lattice. Later on thicker oxide layers will be grown and the blistering of these scales observed. The studies will be extended to technologically important alloys, for instance titanium aluminides. In-situ variable temperature STM will also be used in order to get an atomistic view of the structural properties of the metal-oxide interface. Additionally the results of the STM will be corroborated with studies by LEED, AES, XPS and UPS to get some insight into the long-range order, the elemental composition and the electronic properties of the oxide layer.

5. Growth, Electrical and Electrochemical Properties of Iron Silicides on Iron

It is intended to grow iron silicides on single- and polycrystalline iron by chemical vapor deposition of a SiH_4-H_2 gas mixture at elevated temperatures. The reaction kinetics within the phase boundary region and the diffusion of silicon into the bulk are characterized by thermogravimetry in combination with AES and sputter-depth-profile analysis. Impedance spectroscopy will be used to investigate the electrical and electrochemical properties of the iron silicide films. Later on the iron silicide samples will be exposed to an oxygen atmosphere to grow a passive silicate layer.

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Key Personnel: Strehblow, H.-H., Prof.

Scientific Key Words: Surface analytical methods; Chloridation; Chlorine; Reactive element effect; Heat-resistant steels; X-ray photoelectron spectroscopy; Auger electron spectroscopy

Technical Key Words: Heat exchangers; Waste incineration

SCOPE OF RESEARCH

Fundamental Approach

The main focus of the research is the corrosion behaviour of iron- and nickel-based high-temperature alloys. In the temperature range from 700 to 1000°C, commercial materials as well as model alloys are tested in both oxygen- and chlorine-containing environments. Emphasis is placed on a possible rare-earth effect for the applied aggressive gas mixtures and the influence of pretreatment on the protection properties of some commercial alloys. In collaboration with the J. Stefan Institute, Ljubljana, Slovenia the high temperature corrosion resistance of hard PVD nitride coatings on commercial alloys has been examined.

Specific Topics

1. High Temperature Chlorination Behavior of Inconel 600

This research is supported by the Deutsche Forschungsgemeinschaft. The corrosion behaviour of Inconel 600 is studied for different gas compositions, pretreatments and exposure times at 700°C. From the composition and the distribution of the elements inside the corrosion layer, determined by XPS depth profiling, mechanistic information concerning the chloride attack, and the protective properties of the oxide scales in dependence on their composition, are obtained.

2. The Active Element Effect in Chlorine- and Oxygen-Containing Environments at 700°C

This research is supported by the Deutsche Forschungsgemeinschaft. The influence of reactive elements on the corrosion behaviour of commercial alloys is studied, as well as of some model alloys with different contents of the reactive element. Emphasis lies on alloys with contents of niobium, cerium and yttrium.

3. Thermal Oxidation of TiN and CrN Hard Coatings

This work is performed in collaboration with Navinšek, B., Prof., Dr. and Milošev, I., Dr., from the J. Stefan Institute, Ljubljana, Slovenia and has been supported by the International Bureau of the Research Center Jülich, Germany. The aims of this research program are experimental data and mechanistic information, especially with regard to the corrosion behaviour of CrN and TiN hard coatings on commercial alloy substrates obtained by reactive sputtering at 200°C. The main focus lies on their protective properties against aggressive HCl/O_2 gas mixtures at $T \leq 700°C$.

4. A Closed Specimen Transfer for Surface Analytical Application

This research has been supported by the Deutsche Forschungsgemeinschaft. The aim is the construction and test of a low-cost system for specimen transfer under inert conditions. The developed compact and mobile system allows the specimen transfer from different external preparation stages to the ultra high vacuum of a XPS, UPS, AES and ISS-spectrometer without any significant surface contamination.

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6. Milošev, I., Strehblow, and Navinsek, B., "Comparison of TiN, ZrN and CrN Hard Nitride Coatings: Electrochemical and Thermal Oxidation," Thin Solid Films, 303, 246-254 (1997)

2. High-Temperature Degradation in Aggressive Gases

7. Abels, J.-M. and Strehblow, H.-H., "A Surface Analytical Approach to the High Temperature Chlorination Behaviour of Inconel 600 at 700°C," Corrosion Science, 39, 115-132 (1997).

3. Miscellaneous

8. Abels, J.-M., Hecht, D. and Strehblow, H.-H., "A Closed Specimen Transfer for Surface Analytical Application," Surface and Interface Analysis, 24, 332-338 (1996).

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Scientific Key Words: Computer modeling; Databases; Deposits/heat transfer; Erosion; Erosion-corrosion; Inpurities; In-plant monitoring; Lifetime; Reducing environments

Technical Key Words: Boiler tube failures; Combined cycle system; Fossil-fuel boiler; Steam turbine; Nuclear power systems; Steam generators; In-plant monitoring

SCOPE OF RESEARCH

Fundamental Approach

The Department for Energy has not done fundamental corrosion research as such; rather it does applied research relating to thermal and nuclear power plants: water chemistry of the steam cycles; transport of impurities; chemicals and corrosion products of the steam cycles, failures and lifetime of main equipment.

The Department of Physical Chemistry co-operates with the Department for Energy, and has done fundamental corrosion research: high temperature corrosion of high alloyed and stainless steels in NH_3 and KOH buffered boric acid solutions.

Applications, Engineering Achievements and Technology Transfer

Specific Topics

1. Modelling of Stochastic Processes of Erosion-Corrosion in Thermal Powerplant Equipments

The corrosion and water chemistry database of the units by electrical power of 200 MW, operating in Hungarian thermal power plants was created. The iron corrosion transport model of steam cycles was developed and its simulation program was ready. The research was financed by OTKA (National Scientific Research Fund) and MVM Rt. (Hungarian Electricity Company), Tisza and Dunamenti Powerplant Company.

2. The Modification of Secondary Water Chemistry for NPP Paks

The shell-side corrosion risk factors of WWER-440 steam generators were analysed by the new reliability philosophy of PWR steam generators, and on the bais of this analysis the proposals (change of copper tubes to stainless steel in condenser, initiation of HAVT in working medium) were made to modify the secondary water regime. This modification will be realized in the Paks Nuclear Powerplant, which financed this research, at all units between 1997-2000.

3. The Water Chemistry Expert System of NPP Paks

Six simulating models of Paks NPP (Primary Side: Water Chemistry, Activity Transport; Secondary Side: Ion Impurities, Chemicals and Iron Corrosion Products Transport of Steam Cycles, Mixed-Bed Ion Exchangers) were made and controlled. The computer program of the expert system was made and controlled also; its implementation will be to the NPP net in 1997.

RECENT PUBLICATIONS

1. Õsz, J., Nagy, O., Salamon, T. and Tilky, P., “Reduction, Minimization of the Corrosion Risk of the Steam Generators and the Erosion-Corrosion of the Secondary Side at Nuclear Powerplant Paks,” Second International Seminar on Primary and Secondary Side Water Chemistry of Nuclear Power Plants, Hungary, Balatonfüred, September 19-23 (1995).

2. Õsz, J., “Knowledge Base of the Water Chemistry Expert System for Nuclear Powerplant Paks,” Second International Seminar on Primary and Secondary Side Water Chemistry of Nuclear Power Plants, Hungary, Balatonfüred, September 19-23 (1995).

3. Lipovszki, Gy., "Computer Implementation of the Water Chemistry Expert System for NPP Paks," Second International Seminar on Primary and Secondary Side Water Chemistry of Nuclear Power Plants, Hungary, Balatonfüred, September 19-23 (1995).

4. Õsz, J., "Erosion-Corrosion of the Thermal Powerplant Equipments," Hungarian Energetics, pp42-48 (1996/1).

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Key Personnel:	Bose, S.K., Prof., Roy, S.K., Prof.
Scientific Key Words:	Copper oxidation; Coating durability/adhesion; Coating interfaces; Coating methods; Cyclic oxidation; Laser alloying; Mechanisms; Oxidation at low oxygen pressure; Oxide-metal interface; Point defects; Reactive element effect; Silicides; Iodination; Vacancy annihilation/creation; Void formation during oxidation; Surface analytical methods
Technical Key Words:	Solar absorbers; Fuel cells; Steam generators; Engine materials; Surface engineering

SCOPE OF RESEARCH

Fundamental Approach

The research activities of this laboratory mainly embrace fundamental studies relating to film/scale growth processes on different metal-oxygen and metal-halogen systems, with emphasis on kinetics and growth mechanisms, defect structure of the compounds, transport properties of the different species,adhesion and protective properties of the scales etc. The superimposition of external stimuli such as impressed direct current, impressed static charge and short circuiting across the two reaction interfaces has thrown more light on the role of the interfacial reactions vis-a-vis the inherent physical properties of the growing film/scale and their effect on subsequent growth processes. Novel experimental techniques have been devised to examine changes, if there are any, on the nature of driving forces (Wagner's electrochemical potential gradient and Mott's electrical field gradient) brought about by such external influences. The role of aliovalent dopants in altering the rate of film/scale growth caused by changes in the bulk properties of the reaction products, has also been probed.

Specific Topics

1. Oxidation Kinetics of Copper and Iron under Two Different Modes of Impressed Direct Current, Short Circuiting and Impressed Static Charge

The acceleration and deceleration in the rates of oxide growth on $Cu/Cu_2O/CuO/O_2$ (g) and $Fe/FeO/CO + CO_2$ (g) in a wide range of temperature (973-1173 K), under the two different modes of current application (interrupted and uninterrupted), have established the differential responses of the two reaction interfaces to the scale growth processes. The effect of a shorting circuitry attachment between the M/MO and MO/O_2 (g) interfaces during the scale growth process has normally been reported to enhance the oxidation rate. However, this has been found to be valid only within Wagner's parabolic regime. In contrast, the reverse effect has been observed in the Mott's field-induced parabolic growth region. Static charge application of either kind at one of the reaction interfaces during scale growth process has also brought about changes in the rates. This study has unequivocally established that, without allowing a net electrical current to flow through the growing oxide, modification in the oxide growth rates can be achieved.

2. Iodine Film Growth on Lead and Silver

Tarnishing studies on lead and silver in iodine atmosphere (P_{I_2} = 0.067 - 6.578 kPa) over a wide temperature range (333 - 523 K) have established the defect structures of PbI_2 and AgI to be Schottky-Wagner type and Frenkel type, respectively. In conformity to existing literature, the shorting circuitry attachment between the two reaction interfaces has resulted in enhancement in iodination rates. The kinetic data have been utilized to estimate the potential developed across the iodide layers, diffusivity, concentration of defects, hole and ionic conductivities. The effect of aliovalent elements like Sb and Ag in Pb and Cd in Ag affecting the iodination rates has been explained in terms of defect interactions and transport properties of the defect species.

Applications, Engineering Achievements and Technology Transfer

The main activities centre around development of high temperature coatings to reduce scale loss and improve scale adhesion. However, the emphasis is on the use of superficially applied coatings and coatings developed by laser surface alloying. Studies relating to oxidation behavior of ferritic steels like 2.25-Cr-1Mo and 9Cr-1Mo used for steam generators have also been one of the activities in collaboration with Indira Gandhi Centre for Atomic Research, Kalpakkam.

Specific Topics

1. Development of High Temperature Scaling Resistant Coatings for Plain-Carbon Steels

Plain carbon steels which virtually do not have much high temperature oxidation resistance are invariably subjected to high temperature treatments in air or other oxidizing environments during their various stages of manufacturing processes in steel plants. A number of coating mixtures consisting of various proportions of bentonite, ferro-silicon, ferro-manganese and calcium silicide have resulted in remarkable improvement in reducing scale loss and facilitating scale adhesion.

2. Improvement in Oxidation Resistance of Austenitic Grades Stainless Steel by Superficially Applied Rare Earth Oxides.

AISI-304, -316, -321 and -347 grades of stainless steel are considered to be potential materials of construction for the primary circuit, controlled components, thermal insulations, hot box components etc. in the fast breeder reactors. Such components are invariably subjected to thermal cycling during their service period. Superficially applied rare earth oxide coatings on such steels have shown similar improved oxidation resistance and scale adhesion, as reported for such alloys with elemental rare earth or their oxide dispersoid additions. Similar studies are in progress with AISI-310 grade stainless steel. This investigation is also being extended to c.p. grade Ti and Ti-6Al-4V alloy, where preliminary studies have exhibited promising results even though TiO_2 is known to be a predominantly n-type oxide.

3. Oxidation Behavior of Ferritic Steels for Steam Generators

A detailed study on the effect of microstructural variations of 2.25Cr-1Mo and 9Cr-1Mo steels involving grain size, precipitation of Cr-rich secondary phases brought about by different types of heat treatments as well as welding, on their air oxidation behavior in the temperature range of 773-973K, has been the subject of investigation in collaboration with I.G.C.A.R. Kalpakkam. It is established that tempering treatments, which are normally applied to such steels for improvement in mechanical properties, should be restricted to such time-temperature parameters so that precipitation of Cr-based carbides like $M_{23}C_6$ and M_7C_3 be avoided to retain oxidation resistance.

RECENT PUBLICATIONS

1. High Temperature Oxidation/Iodination

1. Roy, S.K., Seal, S., Bose, S.K. and Caillet, M., "Effect of Superficially Applied CeO_2 Coating on the Non-Isothermal Oxidation of 321 Grade Stainless Steel," Journal of Materials Science Letters, 12, 249-251 (1993).

2. Mitra, S.K., Roy, S.K. and Bose, S.K., "Influence of Superficial Coating of CeO_2 on the Oxidation Behavior of AISI-304 Stainless Steel," Oxidation of Metals, 39, 221-229 (1993).

3. Singh Raman, R.K., Gnanamoorthy, J.B. and Roy, S.K., "Oxidation Behavior of 2.25Cr-1Mo Steel with Prior Tempering at Different Temperatures," Oxidation of Metals, 40, 21-36 (1993).

4. Singh Raman, R.K., Gnanamoorthy, J.B. and Roy, S.K., "Microstructural Variations in the Weldment of 9Cr-1Mo Steel and Their Influence on the High Temperature Oxidation Behavior," Proceedings of National Welding Seminar at Bhilai in December '93, pp12(a)-12(e) (1993).

5. Singh Raman, R.K., Gnanamoorthy, J.B. and Roy, S.K., "High Temperature Corrosion of Weldments of Cr-Moly Ferritic Steels," Proceedings of Symposium on "Welding in Power Plants", at Madras, in February '94, pp57-70 (1994).

6. Kuiry, S.C., Roy, S.K. and Bose, S.K., "A Superficial Coating to Improve High Temperature Oxidation Resistance of Plain Carbon Steels Under Non-Isothermal Conditions," Oxidation of Metals, 41, 65-79 (1994).

7. Seal, S., Bose, S.K. and Roy, S.K., "Improvement in Non-Isothermal Oxidation Behavior of Austenitic Grades of Stainless Steel by Superficially Applied Cerium Oxide Coating," Oxidation of Metals, 41, 139-178 (1994).

8. Kuiry, S.C., Seal, S., Bose, S.K. and Roy, S.K., "Effect of Surface Preparation on the High Temperature Oxidation Behavior of AISI-316 Grade Stainless Steel," Iron and Steel Institute of Japan International, 34, 599-606 (1994).

9. Kuiry, S.C., Bose, S.K. and Roy, S.K., "Development of High Temperature Scaling Resistant Coating for Plain Carbon Steels," Industrial Product Finder, 22, 209-213 (1994).

10. Singh Raman, R.K., Gnanamoorthy, J.B. and Roy, S.K., "Synergistic Influence of Grain Size and Si Content on Oxidation Behavior of 9Cr-1Mo Steel," Oxidation of Metals, 42, 1-21 (1994).

11. Singh Raman, R.K., Gnanamoorthy, J.B. and Roy, S.K., Oxidation Behavior of Microstructurally Different Regions in the Weldment of 9Cr-1Mo Steel," Oxidation of Metals, 42, 31-47 (1994).

12. Roy, S.K., Ananth, V. and Bose, S.K., "Oxidation Behavior of Copper at High Temperature Under Two Different Modes of Current Applications," Oxidation of Metals, 43, 185-215 (1995).

13. Roy, S.K., Bottino, C., Kuiry, S.C., Rakesh, V.R. and Bose, S.K., "Improved High Temperature Oxidation Behavior of AISI 347 Grade Stainless Steel by Superficial Coating of CeO_2," Iron and Steel Institute of Japan International, 35, 433-442 (1995).

14. Kuiry, S.C., Roy, S.K. and Bose, S.K., "Hole Conductivity Estimation in Lead Iodide Film Through Kinetic Study of Tarnishing Reactions," Materials Research Bulletin, 31, 317-327 (1996).

15. Bose, S.K., Mitra, S.K. and Roy, S.K., "Effect of Short Circuiting on the Oxidation Kinetics of Copper and its Doped Varieties in the Temperature Range of 523-1073 K," Oxidation of Metals, 46, 73-107 (1996).

16. Kuiry, S.C., Roy, S.K. and Bose, S.K., "Kinetics and Mechanism of Lead Iodide Film Growth on Lead," Oxidation of Metals, 46, 397-421 (1996).

17. Kuiry, S.C., Roy, S.K. and Bose, S.K., "Kinetics and Mechanism of Film Growth on Lead - Effect of Short Circuiting and Higher Valent Dopant," Oxidation of Metals, 47, 295-315 (1997).

18. Bose, S.K., Mitra, S.K. and Roy, S.K., "Oxidation Kinetics of Copper Under Charge Supply," Transactions of Indian Institute of Metals, 50, 85-96 (1997).

2. Miscellaneous

19. Fasasi, A.Y., Roy, S.K., Galerie, A. and Caillet, M., "Development of Protective Coatings on Ti-6Al-4V by Laser Surface Alloying," Surface Engineering, Vol.1 : Fundamentals of Coatings, Eds. P.K. Dutta and J.B. Gray, Royal Society of Chemistry, Cambridge, U.K., 57-67 (1993).

20. Roy, S.K., Fasasi, A.Y., Galerie, A. and Caillet, M., "High Temperature Oxidation Behavior of Laser Surface Alloyed Iron-Silicon Coatings on Iron," Journal de Physique IV, 3 (Part II) 625-633 (1993).

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Scientific Key Words: Acoustic emission; Coated and uncoated superalloys; Coating methods; Cyclic oxidation; Deposits; Hot-corrosion; Diffusion coatings; Future gas turbine materials; Heat exchanger materials; Intermetallics; Laser alloying; Surface modifications; Thermal barrier coatings; Plasma and arc; Pack cementation; Spallation; Wear; Water vapor

Technical Key Words: Boiler tube failures; Fossil fuel-fired boiler; Gas turbines; Single crystal alloys; Thermal barrier coating systems; Steam generators; Surface engineering

SCOPE OF RESEARCH

The main aim of the high temperature research at the Indian Institute of Technology is to understand the basic mechanisms of degradation of metals and alloys in various industrial applications and train the research students towards high temperature corrosion research. Research projects are assigned to students to carry out basic studies. Three main areas have been concentrated on in the last few years: (a) oxidation research for studying the material degradation in power generating systems, (b) development of high performance materials by surface modification and (c) development of new materials for gas turbine applications. It is unfortunate that the Indian industry does not fund these projects of great importance in the international market. Therefore, the aim of the work remains of academic interest.

Specific Topics

1. Materials Degradation in Power Generating Industry

In the last few years, work is going on to study the degradation behaviour of several superalloys, single crystals. The mechanism of oxidation, hot corrosion, is being studied by carrying out various isothermal, cyclic and short- and long-term tests. Detailed analyses of scale morphologies and composition using sophisticated techniques such as SEM/EDAX, EPMA, SIMS, AES/ESCA leads to understanding of the degradation mechanism (project in collaboration with Research Centre Juelich under Indo-Germany Bilateral Programme).

2. Intermetallics

Oxidation of intermetallics is another important project which is being pursued for the last three years. The studies are being carried out on the alpha2 intermetallics. The effect of Nb has been studied, and the effect of heat treatment, which changes the microstructure, has been investigated with regard to the oxidation behaviour. The effect of quaternary addition to TiAlNb alloys is being studied to achieve the best oxidation resistance.

3. Surface Modification

One of the main works undertaken in the last five years is the surface modification by a laser technique. Mild steel, and ferritic steels, such as 21/4Cr-1Mo and 9Cr-1Mo, have been modified to change their surface composition, which gives not only better oxidation resistance at high temperatures but also better aqueous corrosion resistance. Similarly, 304 stainless steel has been improved by making its surface rich in Mo, to make it better than even commercial available Avesta type super austenitic stainless steels. (The project is being funded by Department of Science and Technology, New Delhi, also in collaboration with the Fraunhofer Institute for Lasertechnik, Aachen, Germany).

4. Failure Analysis

In addition, much work on the failure analysis of boiler tubes, tubes failed due to sulfidic corrosion in petrochemical plants is also undertaken and suitable recommendations are given for future safeguards.

RECENT PUBLICATIONS

Some of the important publications in the last 3 years are given below:

1. Khanna, A.S., Quadakkers, W.J., Yang, X. and Schuster H., "On the Mechanism of Oxidation of NiCrAl Base Alloys in Air and Air Containing SO_2," Oxidation of Metals, 40, 275 (1993).

2. Khanna, A.S. and Desai, V.H., "Corrosion and Oxidation Behaviour of Ti-Al Surface Alloys Formed Using Laser Irradiation," Proc. 12th International Congress on Metallic Corrosion, Sept. 9-14, Houston, Texas, Vol.1, p250, NACE International (1993).

3. Khanna, A.S., Singh Raman, R.K. and Kreutz, E.W., "Oxidation Resistance of Plasma Coated and Laser Treated Mild Steel," in High Temperature Corrosion and Protection of Materials," R. Streiff, J. Stringer, R.C. Krutenat and M. Caillet, Journal de Physique IV, 3, 635 (1993).

4. Pujar, M.G., Dayal, R.K., Khanna, A.S. and Kruetz, E.W., "Effect of Laser Surface Melting on the Corrosion Behaviour of Cr-Plated Ferritic Steel in Acidic Media," Journal of Materials Science, 28, 3089 (1993).

5. Khanna, A.S., "High Temperature Corrosion of Materials," in Metallic Corrosion, Principles and Control, Eds. A.S. Khanna, S.N. Malhotra, K.S.V. Santhanam and M.E. Totlani, M.E, Wiley Eastern, Delhi, pp123-136 (1994).

6. Khanna, A.S., "Recent Approaches to the Understanding of Corrosion," Proc., "New Horizons and Current Opportunities in Chemistry of Materials", organized by USEFI, TIFR, Bombay, Feb. 10-11, pp146-171 (1994).

7. N'gandu Muamba, J.M., Streiff, R. and Khanna, A.S., "The Effect of Chromiumaluminide and Aluminide Coatings on the Oxidation Behaviour of Some Ni-Base Superalloys," in `Materials for Advanced Power Engineering', Part II, Eds. D. Coutsouradis et al., Kluver Academic Publisher, Netherlands, p1335 (1994).

8. Khanna, A.S., Gasser, A., Wissenback, K., Desai, V.H. and Quadakkers, W.J., "Effect of Laser Treatment on the Oxidation Behaviour of Mild Steel Plasma Deposited with Cr+Ni," Journal of Materials Science, 3, 4648 (1995).

9. Khanna, A.S., Coddet, C., Harendranath, C.S. and Anuja, K., "Surface Property Modification Using Vacuum Plasma Technique," Prot, ITSC 95 Conf. on Thermal Spray, Kobe, Japan, 22-26 May, Vol. II, pp577-584 (1995).

10. Pattnaik, A.K., Khanna, A.S. and Wissenback, K., "Oxidation and Corrosion Behaviour of Mild Steel Plasma Coated with Cr and Ni Followed by Laser Treatment," Proc. ITSC 95 Conf. on Thermal Spray, Kobe, Japan, 22-26 May, Vol. II, pp993-1000 (1995).

11. Pattnaik, A.K., Khanna, A.S. Harendranath, C.S., Wissenbach, K. and Goswami, G.L., "Oxidation and Corrosion Behaviour of Laser Alloyed Mild Steel with Chromium," Bulletin of Materials Science, 18, 169 (1995).

12. Prasanna, K.M.N., Khanna, A.S., Ramesh Chander and Quadakkers, W.J., "Effect of θ-Alumina Formation on the Growth Kinetics of Alumina Forming Superalloys," Oxidation of Metals, 46, 465 (1996).

13. Sridhar, K., Khanna, A.S. and Deshmukh, M.B., "Development of Superaustenitic Steels for Marine Applications," Laser Engineering, 5, 107-125(1996).

14. Priya Smpath, Khanna, A.S. and Ganti, S.S., "Environmentally Influenced Degradation of Fibre Reinforced Composites," Materials Performance, 36, 65-69 (1996).

15. Khedkar, J., Khanna, A.S. and Grupt, K.M., "Tribological Behaviour of Plasma and Laser Coated Steels," Wear, 205, 220-227 (1996).

16. Pattnaik, A.K. and Khanna, A.S., "Laser Surface Processing of Cr Coated 9Cr-1Mo Ferritic Steel for Improved Corrosion Resistance," Proc. Int. Conf. on Thermal Spray, STM-10, Singapore 2-4 Sept. (1996).

17. Pattnaik, A.K., Khanna, A.S. and Harendranath, C.S., "Oxidation Resistance of 21/4Cr-1Mo Steel After Laser Surface Alloying with Cr," Metal Forum, 285-292 (1996).

18. Jha, S.K., Khanna, A.S. and Harendranath, C.S., "Oxidation Behaviour of Alpha 2 Intermetallics," Metal Forum, 205-212 (1996).

19. Jha, S.K., Khanna, A.S. and Harandranath, C.S., "Oxidation Characteristics of Ti3AlNb Alloys and Improvement in the Oxidation Resistance by Pack Aluminizing," Oxidation of Metals, 47, 465-493 (1996).

20. Khanna, A.S., Maya, G. and Ramakrishnan, P., "Oxidation Behaviour of C/Al and SiC/Al Composites, Journal of Materials Science, 31 6653-58(1996).

21. Khanna, A.S. and Pattnaik. A.K., “Recent Trends in the Formation of Corrosion Resistant Alloys Using Laser Surface Alloying,” Proc. International Conference on Recent Advances in Metallurgical Processes, IISc, Bangalore, India, D.H. Shastri, E.A. Dwarakadasa, G.N.K. Iyerngar and S. Subramaniam (editors), 2, pp1281-89 (1997).

22. Khanna, A.S. and Pattnaik, A.K., “Recent Trends in the Coatings for High Temperature Applications,” Trans MFAI, 6, 187-206 (1997).

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Scientific Key Words: Oxidation; Acoustic emission; Spallation; Stress and scale behavior

Technical Key Words: Nuclear power systems; Steam generators; Very high temperature heat exchangers

SCOPE OF RESEARCH

Oxidation Under External Stress of 9Cr-1Mo Steel

This research activity is targeted at understanding the high temperature corrosion behavior of steam generator materials. Oxidation by steam/water of the materials leads to generation of scale that impedes heat transfer. Moreover, after crossing a definite thickness, the scale spalls and is carried through the fluid to other vital components of the system where these corrosion products are deposited. The integrity of the scale is also influenced by the external stress experienced by the components. A study is in progress to understand the oxidation behavior of 9Cr-1Mo steel in air for different temperatures and durations with the objective of understanding the scale behavior. In this study, tensile specimens of 9Cr-1Mo steel were subjected to oxidation under an external stress of 40 MPa. The cracking behavior of the scale was monitored by an in-situ acoustic emission technique. Specimens were also subjected to oxidation without application of external stress. The modes of failure of the oxide scale were determined in this way. The data were supported by post-oxidation examination using SEM and EDS. The overall aim of the work is to evolve predictive modes about scale growth so that the schedule of component maintenance by scale removal may be worked out.

RECENT PUBLICATIONS

1. Pillai Rajendran, S., Sivai barasi, N. and Khatak, H.S., “High-Temperature Oxidation of 9Cr-1Mo Steel-Influence of External Stress on the Integrity of the Oxide

Scale," Proc. Symposium on Localized Corrosion Environmental Cracking, January, Kalpakkam, India, paper C-31 (1997).

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Scientific Key Words:	Hot corrosion; Fused salts; Electrochemical measurements; Oxidation
Technical Key Words:	Heat-transfer; Thermal storage; Fuel ash corrosion; Power plant

SCOPE OF RESEARCH

Fundamental Approach

The thrust of the research is on the hot corrosion of metals and alloys in fused salts, with emphasis on their electrochemical phenomena and the role of moisture in influencing the electrochemical reactions related to hot corrosion of metals. The research includes fundamental studies of the understanding of electrochemistry of fused salts, the electrode kinetics of oxide film formation and the role of moisture in affecting those reactions, which enhance hot corrosion of metal in fused salt systems. Fused alkali nitrates and nitrites, widely used as heat-transfer and storage media in the thermal storage system, are the main investigation media in which research has been carried out. An approach is also being made to know the electrochemical role of vanadate ion in increasing the acidity in alkaline sulfates melt and their ultimate effect on hot corrosion of structural metals, with special emphasis on evolving electrochemical understanding of vanadate-induced hot corrosion of metals, relevant to fuel-ash corrosion of power plants.

Applications, Engineering Achievements and Technology Transfer

Most of the laboratory's work is to undertake fundamental studies of electrochemical understanding of hot corrosion of metals in fused salt systems. Besides evolving knowledge for know-how of electrochemical reactions involved in hot corrosion, the expertise employed for the fundamental studies can be utilized in electrochemical screening of the hot corrosion resistance of high-temperature-resistant alloys in various fused salt systems. This can be useful for their selection in fabrication of engineering materials related to power plants.

The fundamental works undertaken are as indicated in the following abstracts .

Specific Topics

1. Electrochemical Understanding of Hot Corrosion of Metals in Fused Nitrates Salt

This research has been carried out at Central Electrochemical Research Institute (CSIR), Karaikudi. The main aim of this work was to understand the cathodic and anodic processes which are responsible for the hot corrosion and protection of metals in fused salt systems. In this study, cyclic voltammetry investigation was carried out on platinum and iron surfaces in sodium nitrate, potassium nitrate and in their mixed melt up to 340^0C. It has been observed that nitrate ion reduction is the main cathodic reaction which determines the extent of hot corrosion while alkali metal oxide formation decreases the cathodic reaction. Formation of highly soluble potassium oxide on an electrode surface in potassium nitrate melt is not able to control the cathodic reaction, while less soluble sodium oxide formation on an electrode surface in sodium nitrate melt decreases the cathodic reaction substantially.

2. Moisture Effect on Hot Corrosion of Metals in Fused Alkali Nitrates Salt

This work was also carried out at Central Electrochemical Research Institute (CSIR), Karaikudi. The overall aim of this research work was to identify and estimate the moisture content and its effect on nitrate ion reduction in the alkali nitrate melt. The moisture content was identified and estimated by observation of the water reduction wave prior to nitrate ion reduction during a cyclic voltammetric study of platinum in wet sodium nitrate, potassium nitrate and in their mixed melt up to 340^0C. Presence of moisture in the melt catalyzes the nitrate ion reduction reaction and also increases the solubility of alkali metal oxides, which are formed on the metal surfaces. This results in an increase of oxidation rate of metals in fused nitrate salts.

3. V_2O_5 Induced Hot Corrosion in Sulphates Melt

A detailed study is being carried to see the electrochemical role of V_2O_5 in catalyzing the oxidation rate of structural metals and nickel-based alloys in an alkali sulfates melt relevant to fuel-ash corrosion of power plants. The main aim of this work is to estimate the extent of hot corrosion of metals in the presence of V_2O_5 in sulfates melt by electrochemical measurements. Emphasis is being placed on understanding the various electrochemical reactions involved between vanadate and sulfate ions which are responsible for the increases of the acidity of the melt. The work still is in progress.

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CONTENTS

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Scientific Key Words:	Ceramic oxidation; Ceramics corrosion; Coal-ash corrosion; Fused salts; Heat exchanger materials; Oxidation/sulfidation; SiAlONs; Silicon nitride; Under-deposit corrosion
Technical Key Words:	Coal-fired boiler; Biomass combustion; Circulating fluidized-bed combustor; Pressurised fluidized-bed combustor; Future gas turbine materials; Ceramic heat exchangers

SCOPE OF RESEARCH

Fundamental Approach

The major interest of the High Temperature Corrosion Group (HTCG) is the application of phase equilibria towards understanding two areas of corrosion science. These areas are: i) the corrosion of metallic and ceramic alloys by corrosive deposits, ii) correlations between the morphological development of corrosion products formed on metallic and ceramic materials and corrosion kinetics. With respect to area i), the group actively seeks to acquire information relating to the establishment of micro-environments at scale/deposit interfaces or, in the case of ceramics, at the corrosion product/material interface. To this end, fundamental research programmes in progress investigate chemical interactions between metallic materials and 'dry' alkali metal and alkaline earth metal sulphates and between silicon - based ceramic materials and molten alkali metal sulphates. Work related to area ii) involves careful determination of corrosion product chemistry and phase assemblage after various periods of corrosion. The HTCG has extensive knowledge and experience of phase relationships in M-Si-Al-O-N (M=Y or rare earth) systems and is able to apply this in developing an understanding of the manner in which corrosion products form during oxidation or molten sulphate corrosion of silicon nitride - based ceramics. The group also has interests in the reactive element effect as a method of reducing the tendency for Ni-Cr alloys to undergo catastrophic sulfidation/oxidation corrosion. A further interest of the group is standardised oxidation and corrosion test procedures for materials, in particular structural ceramics.

Applications, Engineering Achievements and Technology Transfer

The HTCG's activities are geared toward emulating corrosion effects observed in real systems. Thus the studies of interactions of materials with 'dry' and molten deposits relate to corrosion environments likely to arise in coal-fired boilers (pulverised, fluidised bed, circulating fluidised bed) and in combined cycle systems. The studies pertaining to ceramics relate to US and Japanese initiatives in developing ceramic gas turbines and toward developing simple materials screening experiments. As indicated below, work is frequently conducted in association with other European Universities / Laboratories or with European or Irish Industry.

Specific Topics

1. *Corrosion of Boiler Steels by Alkali-Metal Sulfates at Temperatures in the Range 400 to 650°C*

This research project forms one aspect of a much larger research program financed by the Human & Capital Mobility programme of the European Union. Nine other European partners are involved in this program which is investigating the oxidation, carburisation, sulfidation, oxidation-chloridation, and deposit corrosion of more recently developed 9 and 12% Cr ferritic steels. The work at Limerick focuses on the interactions between these materials and alkali-metal sulphate deposits in a gas environment corresponding to that produced by the combustion of brown coal. Corrosion morphologies typical of those observed on corroded boiler tubes can be produced by the testing techniques employed. Work is in progress to determine differences in corrosion rates of these materials and how their performance compares with austenitic stainless steels Type 304 and Incoloy 800.

2. *Oxidation and Corrosion of Silicon Nitride and SiAlONs in Gaseous Environments*

This work has been conducted in conjunction with the University of Northumbria at Newcastle (UK) under the Brite Euram programme of the European Union. Industrial endorsers of the project were T & N Technology (UK) and British Gas. Materials investigated were RBSN and HIPped silicon nitride (supplied by T&N) and β-sialon materials with z-values ranging from 0.2 to 3.0 which were fabricated at Limerick. Environments employed in the corrosion test programme included laboratory air, chloridising/oxidising, sulfidising and simulated flue gases. Experiments at temperatures of 1150 and 1350°C were conducted for times of up to 1000 hours. The major conclusion from this program was that a z=3.0 material was the only one which could withstand corrosion in all of the four environments. In the oxidising and oxidising/chloridising environment the HIPped and RBSN materials performed well. From the work conducted at 1350°C, it has been possible to elucidate the mechanism by which the materials oxidise/corrode and why each of the gaseous environments give different degradation rates. Similar effects have been observed for these materials containing 10% (by weight) silicon carbide ie. SiN - SiC composites. In rationalising the results obtained from these corrosion studies, the HTCG used its extensive experience relating to glass formation and crystallisation in M-SiAlON systems together with its knowledge of phase relationships in these systems.

3. Chemical Degradation of Silicon Nitride-Based Materials by Molten Alkali-Metal Sulfates

This work, which is sponsored by the University of Limerick is investigating the chemical degradation of the silicon nitride materials referred to above by molten sodium, potassium sulfates. The work involves complete immersion of coupons of the ceramics in the sulfate in air or in a gas containing sulphur dioxide at a temperature of 1150°C. Of the materials tested, only a z=3.0 b-sialon has sufficient corrosion resistance to withstand such aggressive environments and this material has been tested for up to 360 hours with encouraging results.

4. Reactive Element Effects for Chromia Formers in Sulfidation/Oxidation Environments

This project investigates the corrosion of Inconel 690 and 617 alloys in calcium sulphate - carbon mixtures. By suitable manipulation of the calcium sulfate to carbon mole ratio, it is possible to induce catastrophic sulfidation/oxidation corrosion in these nickel - based alloys within 24 hours at temperatures in the range 750 to 950°C. Results obtained show that pre-oxidation of these alloys reduces extents of corrosion slightly. If, however, coupon surfaces are lightly coated with yttria prior to pre-oxidation, sulfidation/oxidation corrosion can be completely prevented in the temperature range 800 to 900°C.

5. Commercially Sensitive Industrially-Based Projects

The University of Limerick was established to provide technical support to Irish Industry and to provide a R&D infrastructure which could assist multi-national enterprises which operate in Ireland. To this end the HTCG has conducted a two year programme of oxidation and corrosion testing for Garret Ireland (Allied Signal). In addition, the group has assisted Shannon Turbine Technology with investigations into

Pt-Al coating application techniques and plasma sprayed bond coat reliability. The duration of these two projects was one year.

Collaborators

Human & Capital Mobility Network (Corrosion of boiler steels)

Grabke, H., Prof. (network leader) (MPI Dusseldorf), Stott, F.H., Prof. (UMIST), Gesmundo, F., Prof. (Genoa), Pieraggi, B., Prof. (Toulouse), de Wit, H., Prof. (Delft), Shutze, M., Dr. (DECHMA), Norton, J., Mr. (JRC Petten), Quadakkers, J., Dr. (KFA Julich), Trujillo, F., Prof. (Un. Complutense, Madrid).

Corrosion of Ceramics

Datta, P.K., Prof. (University of Northumbria at Newcastle).

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ISRAEL

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Scientific Key Words: Alloy oxidation; Grain boundary diffusion and interdiffusion; Void formation during oxidation; Intergranular oxidation; Intermetallics; Pesting; Metal dusting

SCOPE OF RESEARCH

Specific Topics

1. *A New Model of the Pest-Like Disintegration of Intermetallics Due to Intergranular Oxidation*

A new, diffusional model of disintegration of intermetallics during oxidation has been developed. The model is concerned with intermetallics, such as $NbAl_3$, in which the pest phenomenon occurs due to intergranular oxidation. It is assumed that in these cases oxidation leads to an excess of vacancies at grain boundaries. The migration of the excess vacancies to the surface facilitates the diffusional growth of grain boundary cracks. The steady-state vacancy concentration ahead of the crack tip is found from the diffusional equation comprising the vacancy sources and sinks. The rate of crack propagation is found through the vacancy flux to the crack tip. Two different steady-state regimes of crack growth (fast and slow) are established, and the temperature of transition from one regime to the other is determined. The fast regime is related to the disintegration of intermetallics containing a substantial number of structural vacancies. The slow regime corresponds to the case when no disintegration occurs. The rate of diffusion crack propagation is only slightly affected by the gradients of the internal stresses and of the equilibrium vacancy concentration in the oxidation zone. The decisive role of the vacancy excess generation in the fast crack diffusion propagation is revealed. Activation energies of the process are estimated.

2. The Mechanism of Disintegration During Metal Dusting

The process of catastrophic carburization known as 'metal dusting', whereby a solid metallic material is converted into fine particles in a carburizing atmosphere, has been analyzed. It is shown that this conversion is the result of plastic deformation and subsequent fracture accompanying diffusional phase formation in the near-surface layer. The process is controlled by internal stresses arising during phase transformation. Competition between stress generation and relaxation may result in attaining ultimate strength in the near-surface layer and its fracture. Such a mechanism of metal disintegration may occur in a certain temperature interval, depending on the kinetic and geometrical parameters of the system - the diffusivities of the alloy's components, the ratio between specific volumes of the new and the old phases, and the ultimate plastic strain. The temperature interval for disintegration of carbon steel, the rate of disintegration, and the period of the disintegration cycle, are evaluated and compared with experimental data.

3. Penetration of Oxygen Along Grain Boundaries During Oxidation of Alloys and Intermetallics

Fast penetration of oxygen into grain boundaries and intergranular oxidation of β-NiAl have been observed. Since the solubility of oxygen in NiAl is virtually nil, special ways of oxygen ingress at grain boundaries have to be presumed. Selective intergranular oxidation of binary alloys and fast penetration of oxygen along grain boundaries are analyzed by computer simulation. Interdiffusion caused by consumption of the less noble component by oxidation at the metal/oxide interface leads to deviation of the alloy composition from the original value. When the diffusivity of the less noble component is higher than the diffusivity of the other component, a grain boundary Kirkendall effect may lead to void chain formation. Experimental evidence for this phenomenon is presented. The deviation in composition and void formation are considered as processes influencing the effective oxygen diffusivity. Both processes are found to allow penetration of oxygen as fast as grain boundary interdiffusion occurs. In addition, oxygen penetration during intergranular internal oxidation when oxides form at voids beneath the metal/oxide interface is analyzed and treated as a self-propagating process. In this case, fast oxygen penetration is accompanied by fast internal oxide formation and fast displacement of the metal/oxide interface.

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ITALY

Contents

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Scientific Key Words: Oxidation/sulphidation; Cyclic oxidation; Hot corrosion; Deposits/heat transfer; Salt deposits; Reducing environments; Bond/thermal barrier coatings; Burner rigs; Ceramics corrosion; Coal-ash corrosion; Coated and uncoated superalloys; Corrosion-mechanical property interactions; Gasification; Heat exchanger materials; Intermetallics; ODS alloys; Probes; Silicon carbide/combustion atmosphere; Waste incinerator materials

Technical Key Words: Oil-fired boiler; Coal-fired boiler; Advanced steam conditions; Atmospheric pressure fluidized-bed combustor; Condensate (dew-point/downtime) corrosion; Waste incineration; Very high-temperature heat exchangers; Land-based gas turbines; Thermal barrier coating systems; Coal gasification; Syngas coolers; Heat exchangers

SCOPE OF RESEARCH

Fundamental Approach

The unavailability of ENEL thermal power plants, due to fireside corrosion problems, is estimated to be less than 1% of its overall value, even if it is believed that their exploitation under cycling conditions and the construction of multi-fuel boiler (oil, coal and gas) could increase the previous figure as a consequence of a major impact of fireside corrosion on material stability. Furthermore, in the medium future, gas turbines operating at high temperature will be extensively used for power generation and also for repowering some steam boilers. The aims of the research activity are the assessment of high temperature corrosion behavior of traditional and advanced materials to be used for the construction of the most critical components of power plants, and the evaluation of their resistance to corrosion in the operative environments. Moreover, the acquisition of basic knowledge is very useful for a proper choice of technical alloys, so that ENEL is engaged both in fundamental and experimental studies as concerns the behavior of carbon steels, low alloy steels, alloyed steels, stainless steels, nickel and cobalt based superalloys, ODS alloys, ceramics materials and metallic and ceramic coatings. The main components examined are: conventional and advanced combustors and/or boilers, land-based gas turbines, coal gasification and waste-to-energy systems. Careful attention is devoted to simulate in the laboratory the operating conditions accurately in order to obtain a better understanding of corrosion damage mechanisms. So the experimental research concerns the combustion gas thermochemistry, formation of aggressive deposits on suitable specimens, influence of deposits and/or gaseous species on the stability of bare alloys, dependence of the corrosion mechanisms on heat flux, and of coating and protective oxide- scale integrity on thermal cycling and mechanical damage due to fatigue and creep. ENEL is also participating in the project “Discontinuous corrosion testing in high temperature gaseous atmospheres”, supported by The European Community in the frame of the Fourth Framework Program, and aimed at standardizing high temperature corrosion tests.

Applications, Engineering Achievement and Technology Transfer

Most of the experimental activities are addressed to assess the choice of structural and process materials, collect engineering data on their resistance to corrosion in simulated and true operating conditions, develop procedures for the prevention and control of corrosion, and guidelines for a correct exercise of thermal power plants, and define suitable models, which allow estimation of the service life of the most critical components in the energy production field. The work is often done in cooperation with industrial partners, Universities and other Research Institutes such as CISE and the Institute for Advanced Materials of Joint Research Center of the European Community.

Specific Topics

1. Corrosion of Materials for Fossil-Fired Boilers

The behavior of candidate materials, to be adopted for the superheaters of the steam advanced cycles in the fossil-fired thermoelectric power plants, is examined. Corrosion tests concern the low alloy steel grade T22, medium alloy steels grades T91 and E911, and stainless steels types 304SS and 347SS, and are usually performed by simulating heat fluxes through the use of suitable probes. The surface of specimens is sprayed with alkali sulfates or with sulfate/vanadate salt mixtures before starting each test.

Generally temperature ranges from 540°C to 650°C and the influence of different amounts of SO_2, SO_3 and HCl is examined.

2. Corrosion of Materials for Very High Temperature Heat Exchangers

This specific activity is carried out in the framework of the European COST-501 R III Program. The behavior of ODS alloys types MA956, PM2000 and ODM 751 are performed at temperatures ranging from 850°C to 1100°C and specimens are exposed to oxidizing gaseous atmospheres. Tests are carried out using as-received specimens and specimens with the surface contaminated by sodium sulfate. Specimens of ODS alloys are also exposed to flue gas in a propane fuelled combustor at 1200°C and daily cycled to room temperature.

3. Corrosion in Reducing Atmospheres

This activity is mainly performed in the framework of the COST-501 R III Program with the aim of assessing the corrosion performance of ODS alloys and some other commercial alloys such as Alloy 800H and Sanicro 28 under Downtime Corrosion conditions. Specimens are exposed to simulated Coal Gasification Atmospheres at temperatures of 350°C and 500°C, and cycled to room temperature at 100 hour intervals. The test duration is of about 1000 hours and operating atmospheres are simulated using gaseous mixtures of H_2, CO, H_2S, HCl and H_2O. After the 1000 hour period of exposure to the high temperature atmosphere, the specimens in form of sheet are subjected to mechanical stress. Then they are exposed to moist air for a period of 720 hours in order to verify if pitting and/or stress corrosion cracking occurs. ENEL is also studying the behavior of carbon and low alloy steels under atmosphere simulating combustion with low NO_x content and different water concentration. Tests with a length of about 1000 hours are performed at temperatures up to 500°C. The resistance to corrosion of the same steel is also evaluated when oxidizing atmospheres are cyclically replaced by sulfidizing ones, in order to develop a suitable method able to restrain corrosion attack when the concentration of H_2S is significant.

4. Corrosion of Materials for Land-Based Gas Turbines

The resistance to oxidation in sulfur-containing atmospheres and to type-I/II hot corrosion of nickel and cobalt base superalloys, coatings and thermal barriers employed for blades and vanes of gas turbines is evaluated, and the attack morphology is examined, in order to rank the performance of different materials and coatings. Superalloys such as IN738, IN792, IN939, U510, U520, X45, and FSX-414, as received and coated with MCrAlY, Al, Al/Si (11%) and YPSZ, YPSZ SiO_2 sealed thermal barriers are tested at temperatures ranging from 700°C to 1000°C. The oxidation tests are performed using a three horizontal furnace corrosion test circuit, while the hot-salt corrosion tests are performed in a low-velocity burner rig, based on VAMAS guidelines, and in a rig using the 'Dean test' methodology for condensing Na_2SO_4 vapours on the specimen surface. Tests simulating heat-flux conditions with a gas temperature of about 1300°C are also performed. A small experimental activity is devoted to the characterization of TiAl intermetallic alloys. High temperature corrosion/deformation in the creep regime and in creep/fatigue regime tests at temperatures ranging from 850°C to 900°C are also carried out in oxidant sulfur-containing atmospheres, with and without salt addition, on IN738 and U520 superalloys as received and coated with MCrAlY.

5. Corrosion in Case of Cofiring RDF and Coal

At present, ENEL has a small technological observatory aimed at acquiring the state-of-the-art as concerns the boiler materials implications of cofiring a fraction of municipal waste, with coal in utility boilers designed to burn coal, and the effect of excessive boiler fouling on the plant performance. At any rate, ENEL has developed a suitable probe to evaluate through in-field tests with resistance to corrosion of boiler materials when RDF is cofired with coal.

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2. Corrosion of Materials for Very High Temperature Heat Exchangers

4. De Gaudenzi, G.P., Uberti, F., Bregani, F. and Toledo, G.P., "ODS Alloys for High Temperature Heat Exchangers - Evaluation of Corrosion Resistance of MA956 and

PM2000," Proc. Materials for Advanced Power Engineering 1994, Liège (B), October 1994, Eds. Coutsouradis et al., Kluwer Academic Publishers, Dordrecht (NL), 1563-1572 (1994).

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3. Corrosion in Reducing Atmospheres

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Scientific Key Words:	Alloy creep relaxation/cracking; Carburization; Centrifugally cast alloys; Coating methods; Eddy current; Life prediction; Ultrasonic attenuation
Technical Key Words:	Ethylene pyrolysis; Steam reforming; In-plant monitoring

SCOPE OF RESEARCH

Fundamental Approach

The aim of this research is the evaluation of the damage due to creep on the tubes installed in the radiant zone of steam reforming furnaces, and the evaluation of the degree of the damage due to carburization on the tubes installed in the radiant zone of thermal cracking furnaces.

In the case of the steam reforming tubes, the earliest and more frequent rupture is normally due to the creep-damage as a consequence of local overheating brought about both by anomalies of the burners' flame and catalyst plugging that reduces the gas flow inside the tubes.

The creep-induced cracks are nucleated somewhere in the material comprised between the half thickness and internal surface, and they grow both towards the internal and the external surfaces till mechanical collapse.

In a steam-reforming furnace, operating under pressure, if a tube fails during service, it must be put out of the service: if on-line crimping of the corresponding pigtail is not feasible for either technical or safety reason, plant shutdown cannot be avoided, with associated heavy production losses and shutdown/startup costs.

The need of an effective in-service inspection technique for early and reliable detection of creep damage in reforming tubes is obvious.

In the case of thermal cracking furnace tubes, the cracking reactions lead to coke formation as an adherent layer onto the internal surface of the tubes. In ethylene cracking furnaces this layer is removed at regular intervals by burning it with a steam and air mixture: such an operation is currently called decoking.

Regular production and decoking induce a cycle pattern of shot oxidizing (decoking) and long carburization periods, in which carbon diffuses into the metal matrix.

Beyond a certain level of carburization, the tubes may unexpectedly fail on the basis of different mechanisms: in the case of HK40 alloy, the failure is usually due to creep (the internally carburized layer is characterized by greater specific volume compared with that of the original material, which fact causes additional stresses affecting the periphery of the tube) and sometimes leads to reduction of the wall thickness due to metal dusting. Regarding the alloys with higher nickel content (HP40, MAN 36X, 36X), the failure more commonly found is represented by circumferential cracks due to the increased brittleness of the material.

Materials saving, effective spare part management and avoiding unnecessary maintenance costs, come out as the more relevant motivations for in-service inspection of cracking furnace tubes.

Applications, Engineering Achievements and Technology Transfer

Ultrasonic (UT) in-service inspection of steam reforming tubes, to assess the degree of damage due to creep, has been successfully carried out.

The physical principle is represented by UT beam transmission through the tube wall. A pair of separate emitting and receiving transducers are coupled to the tube walls by means of a water feed. The attenuation of the transmitted beam increases with the density and the stage of development of creep fissures.

Together with UT beam transmission techniques, a low frequency eddy current test method is under investigation. The use of a proper winding for the probe, as well as the development of computerized equipment with dedicated software, is the aim of the research, in order to obtain a reliable detection of cracks without significant interference due to the extenral oxixe layers or the residual magnetism typical of the high nickel alloys.

The eddy current technique can be considered an important option, having the great operative advantage not to require liquid coupling, but the accuracy and the sensitivity should be similar to those guaranteed by the UT technique.

In the case of the carburization on the tubes installed in the thermal cracking furnaces, such as those of ethylene plants, tube integrity evaluation is strictly related to a precise and reliable measurement of the carburization depth. The reliability of both inspection equipment and damage grading have been achieved in a satisfactory way. However, some more efforts are required in order to improve the accuracy of the measured carburization depth.

Moreover, a research program has been initiated to investigate the effect of aluminum and ceramic coatings to counteract the carburization of the tubes in the ethylene cracking plants.

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Technical Key Words: Gas turbines; Energy plants; Fossil fuel-fired boilers; Furnace wall corrosion; Waste-fired boilers

SCOPE OF RESEARCH

Fundamental Approach

1. Once activity is aimed at identifying the eventual effects of the application, by vacuum plasma spray, of overlay coatings, on the properties of nickel-based superalloys, used in land-based gas-turbine buckets. It is focused on commercial alloys and coating processes, used for ENEL's plant fabrication. In particular, fatigue, creep, thermal shock and corrosion in Na_2SO_4 tests, together with optical and electron microscopy examinations, are performed on as-machined and coated specimens, and the observed properties are compared.

2. In the second research, a probe has been developed for the measurement of fire-side corrosion in thermal power plants, that has the aim to simulate the behavior of waterwall tubes in contact with combustion gas. The probe is made of the same material as the waterwalls, and is kept at the same temperature as the boiler tubes near them by an air-cooling system. The probe is installed in the boiler through a hole between two tubes, having a very little diameter which does not need any

cutting and does not straddle the tubes. After the planned exposure time the probe is extracted; a platinum plug applied in the surface allows the measurement of the thickness loss. This can be done either by direct measurement with a roughness-meter after descaling of the probe surface, or by SEM observation of the metallographic cross-section, including the scale elements' analysis. The probe design allows also the measurement of heat flux and gas sampling for in-field analysis of the concentration of the main species in flue gas that can be related to corrosion phenomena (O_2, H_2S, CO, SO_2 etc).

Applications, Engineering Achievements and Technology Transfer

1. In the first research, it is well known that the application of coatings implies complicated processes of microstructural transformation on the underlying base metal, due both to the thermal cycles, during deposition and subsequent heat treatments, and to compositional changes, that may continue during service, close to the coating. Such processes may alter the complicated equilibrium of the microstructure, on which the strength of the material depends. The subject of the investigation is thus crucial, with respect to the availability and reliability of the gas turbines for energy production, the importance of which is now enhanced by the increasing popularity of the combined cycle plants.

2. In the second investigation, the probe has been established for the study of the risk of the sulfidation attack in reducing atmospheres in boilers equipped with primary low-NO_x measures (low-NO_x burners, BOOS, OFA, Reburning etc), and corrosion monitoring is performed in ENEL power stations since 1990. The next applications of this technology are planned in tests of combustion or Orimulsion, and in a test of cofiring of refuse-derived fuel and coal, that will be undertaken in conjunction with some other European partners.

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Technical Key Words: Coal-fired boiler; Oil-fired boiler; Coal gasification

SCOPE OF RESEARCH

Fundamental Approach

The primary aim of the studies carried out in this period was to develop a better understanding of a number of basic aspects in the corrosion of simple metallic materials at high temperatures. These included a number of different subjects such as:

1. A critical examination of the kinetics of scaling in the corrosion of binary alloys by a single oxidant.
2. The effect of the reactions at the interfaces between the scale and the gas on the overall rate of corrosion of pure metals and alloys.
3. The critical content of the most-reactive component for the transitions between the various fundamental scaling modes of binary alloys.
4. The prediction of the scaling modes of binary alloys between components presenting a limited reciprocal solubility (LSBA).
5. The kinetics of oxidation of LSBA by a single oxidant forming only the most-stable oxide as an external scale.
6. The kinetics and morphology of internal oxidation of LSBA in the presence or not of external scales.

The experimental studies involved the search for materials with an improved resistance to high-temperature corrosion in purely sulfidizing gases and in mixed oxidizing-sulfidizing atmospheres of high sulfur and low oxygen activities, such as those involved in coal gasification processes. Additions of metals such as Nb, Y and Ce have been tested and are partly still under examination. A number of studies involved examination of the scaling behavior of commercial materials, such as low and medium-chromium steels, under conditions of thermal or chemical cycling, simulating conditions which may arise in the operation of industrial boilers, but also of the corrosion of intermetallic materials within the systems Fe-Al, Ni-Al and Ti-Al in various environments. Finally, many studies examined the corrosion of simple LSBA by a single oxidant (either oxygen or sulfur) to examine the effect of the low solubility of the two components, and of the presence of two metal phases, on the scaling behavior of these materials, to be compared with the theoretical models which have been developed simultaneously.

Applications, Engineering Achievements and Technology Transfer

A number of the studies developed in this period concerned various materials which are used, or could be used in systems of relevance for practical applications, such as in the operation of coal- fired and/or oil-fired boilers or that of coal gasification plants, as specified below. Most of these works have been developed in collaboration and with financial support by industrial partners such as the Italian Electricity Generating Board (ENEL) or the Centre for Development of Materials (CSM). The objective of these works was to establish the kinetics of scaling of materials under the conditions examined as well as the related mechanisms. The information obtained is of interest for the related technologies. Other researches of more fundamental approach, part of which has been supported by the European Community through a number of specific Contracts, are not of immediate interest for practical applications.

Specific Topics

1. Corrosion of Various Ferritic Steels Under Conditions Relevant to the Operation of Industrial Boilers

This work, mainly developed in collaboration and under Contract by ENEL, concerned various aspects of the scaling of plain and low and medium-chromium steels used in the construction of coal-fired or oil-fired industrial boilers, including corrosion in combustion gases of an oxidizing type under thermal cycling conditions and corrosion under isothermal conditions but in atmospheres whose composition was changed cyclically from oxidizing to sulfidizing conditions. The latter study was intended to simulate situations which may arise when the boilers are operated by means of a two-stage process recently developed to reduce the NO_x emissions. The results of the tests carried out at 500°C showed that initial oxidation of samples does not offer a good protection against following sulfidation, even of short duration. The initial oxide scales are easily penetrated by sulfur with a substantial increase in the scaling rate. Similar studies have been carried out more recently within the framework of a collaborative program between 10 laboratories of 7 different countries, funded by the European Community (Human Capital and Mobility). The materials tested were two 9 Cr and two 12 Cr ferritic steels exposed to a number of cycles (up to 4) of 24 hr each at 600°C. Cyclic corrosion, starting with an oxidizing cycle, produced scales presenting alternate layers of oxides and sulfides, while the rate was intermediate between that of pure oxidation and pure sulfidation. The results of cycles starting with oxidation have not yet been examined.

2. Corrosion of Intermetallic Materials in Various Corrosive Environments

These studies included the corrosion of a number of alloys in the Fe-Al, Ni-Al and Ti(Nb)-Al systems under different operating conditions (generally combustion gases in the presence or not of salt deposits) in order to assess the possibility of using these materials for various industrial applications at high temperatures. Most of this work has been developed in collaboration and under Contract by the Centre for Development of Materials (CSM). Testing of FeAl, with and without Y_2O_3 additions in atmospheres of coal combustion, showed a very good resistance of these materials at 600 and 700°C, while the hot corrosion resistance of both Fe_3Al an FeAl at 600°C was not very good. Corrosion of both Ni_3Al and $(Ti,Nb)_3Al$ in a simulated combustion gas with and without salt (Na_2SO_4/NaCl mixtures) deposits at 600-800°C showed a rather good resistance to the gas, but a considerable acceleration of the corrosion rate in the presence of salts.

3. Effect of the Addition of Refractory or Reactive Elements on the Corrosion Resistance of Base Metals

The aim of these studies was to examine the possibility to improve the corrosion resistance of base metals such as Fe, Co and Ni to atmospheres of high sulfur activity, and/or low oxygen activity, such as those involved in the operation of coal gasification plants, by means of additions of a second component having a good resistance to sulfidation. For this, niobium additions have been tested first, and then additions of reactive metals such as yttrium or cerium, which are expected to be also resistant to high-temperature sulfidation. This work has been supported by the European Community through specific Contracts involving collaboration with partners from outside Europe. Main coworkers have been: Rizzo, F.C., Prof., of the Department of Materials Science and Metallurgy of the Pontificia Universidade of Rio de Janeiro (Brazil) and Wu, W.T., Prof. and Niu, Y., Dr., of the Institute of Corrosion and Protection of Metals of the Academia Sinica in Shenyang (China). The results showed that generally these alloys are much more resistant than the base metals to sulfidation and sulfidation-oxidation, even though the corrosion rates are still too high for additions of the refractory or reactive elements up to 30 wt%. Moreover, in no case it has been possible to prevent the formation of an outermost layer of the sulfide of the base metal completely. These studies are also of interest as examples of scaling of binary alloys forming intermediate phases.

4. Scaling Behavior of Simple Two-Phase Binary Alloys by a Single Oxidant

The materials studied in this field include a number of simple binary alloys involving metals presenting a low reciprocal solubility and forming only the two terminal solid solutions, because this is the simplest situation which may arise for alloys presenting a solubility gap. The systems examined so far, or still under examination, include the corrosion by oxygen and/or by sulfur of alloys such as Cu-Ag, Cu-Co, Cu-Cr, Cu-Fe etc. The results of these studies have been compared with the theoretical predictions developed simultaneously for some special situations in the scaling of two-phase alloys and have been of help in understanding the complex processes involved in the corrosion of these materials. While these studies do not have an immediate relevance for practical applications, they can contribute to provide a better basis for understanding the scaling behavior of multicomponent, multiphase materials useful for high-temperature applications, such as coatings, which may eventually result in materials improvement. These studies involved to a different extent also scientists from other laboratories, already listed above.

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Scientific Key Words:	Electrochemical measurements; Oxidation at low oxygen pressure; Sensors; Oxide-metal interface; Nucleation
Technical Key Words:	Electrical resistors; Electrochemical microsensors; Heat treating equipment; Heating elements

SCOPE OF RESEARCH

Fundamental Approach

The aim of the research is to study the reactivity of materials towards oxygen at high temperature and low oxygen partial pressures. The research includes the measurements of the oxidation kinetics, by means of non-conventional apparatus, under well defined values of temperature and oxygen pressure. The experimental set-up consists of a micro chamber where the sample is located and with a system of electrochemical oxygen sensors which allow the measurements of the oxygen partial pressure. The oxygen activity is measured along the stream line, at the entrance and at the exit of the microchamber. Through a mathematical algorithm, the E.M.F. of the sensors may be used to evaluate the number of oxygen moles that reacts with the sample and, therefore, the kinetics.

Preliminary measurements have been carried out on carbon in the form of: graphite, glassy carbon, fullerene C_{60} and synthetic diamond. Successively the oxidation of titanium carbide was also studied. The reliability of the new experimental method has been verified by oxidising a copper foil for which the oxidation kinetics, in the same range of pressure an temperature, was already known from a different method.

Experiments were also performed for studying transport properties of oxides at high temperature. In this experiments the oxide/oxygen-gas system is displaced from the equilibrium by a temperature-jump. Then, the relaxation of the conductivity, due to the new condition, is measured as a function of time. An appropriate analysis of the conductivity-time curve allows the evaluation of the activation energy for ionic conduction.

Application

The work mainly deals with the study of the metal-oxide interfaces. Concerning technology, there is interest in the possibility of producing metal-ceramic junctions by growing a compact oxide layer at the common interfaces.

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Scientific Key Words: Hot corrosion; Salt deposits

Technical Key Words: Future gas turbines materials; ODS alloys

SCOPE OF RESEARCH

Fundamental Approach

A small group is interested in hot corrosion behavior of metallic superalloys in gas turbine and in waste incinerators environments. The overall aim of the work is on the setting-up of laboratory method able to provide a continuous contaminant deposition on the samples during the hot corrosion tests. The research includes studies of the corrosion resistance of metallic alloys in conditions similar to the operating conditions of an oil-stoked gas-turbine, where molten salts arising from the fuel may be deposited. We have worked for some years at the laboratory in this field using the method of spraying once the contaminant on the samples before the high temperature tests, but the experimental results do not always correspond to the data arising from the service. After about 24 hours the corrosion rate is constant, as if the salt is consumed. In order to set up a more reliable method able to provide more valid data, a device has been assembled in which a continuous deposition of the contaminant is supplied onto the surface of the samples during the corrosion tests.

Applications, Engineering Achievements and Technology Transfer

The studied method is apparently similar to that proposed by Dean in 1961 and exploits a two independently controlled furnaces. In the first section the contaminant evaporates and is carried by an inert gas in the second colder section; the temperature decrease produces the condensation of the contaminant on the sample, assuring the continuous deposition also in the long-time tests. The experimental data obtained by using various metallic alloys, shows that in the hot corrosion tests the continuous deposition of the contaminant is able to provide substantially different data than those obtained by once contaminant spraying. The difference between the data obtained by once spraying and by continuous deposition, at the same temperature and in the same gaseous atmosphere, is approximately a factor of three for all the metallic alloys considered. This method is also able to provide the continuous deposition of undissolvable water contaminants (V_2O_5, vanadates etc.), contrary to the method proposed by Dean, and may be advantageously employed in the hot corrosion tests.

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Scientific Key Words: Coatings; Intermetallics; Ion implantation; Spallation; Surface analytical methods; Thermal cycling; Thin layer activation

Technical Key Words: Airframe materials; Engine materials; Fuel cells; In-plant monitoring; Surface engineering

INTRODUCTION

The Joint Research Centre (JRC) is the corporate research laboratory of the European Union. It is established by the European Commission (EC) with headquarters in Brussels, Belgium. The JRC objectives include the provision of independent scientific and technical expertise to Community institutions and support for the implementation of Community policies and activities; to make JRC capabilities and (special) scientific and technical installations available to public and private bodies; and to contribute to the reduction of scientific and technological differences between Member States. The JRC is increasingly engaged in competitive activities, including shared cost actions. The JRC is located in five separate sites; the largest one is in Ispra, Italy. One of its seven institutes is the Institute for Advanced Materials (IAM) located in Petten, The Netherlands and in Ispra, Italy. Besides 250 permanent staff members, the IAM hosts approximately 50 visiting scientists, post doctoral fellows and post graduate students. One of the activities in Ispra is surface degradation studies, including high temperature corrosion. Within this activity, which was expanded significantly over recent years, emphasis is put on external collaborations and advanced techniques, which would normally lie outside the scope and capabilities of national organisations.

SCOPE OF RESEARCH

Specific Topics

1. Ion Implantation as a Tool for High Temperature Corrosion Studies

Ion implantation offers the advantage of adding an element to a surface layer in a fast, well controlled and reproducible manner. Also due to the fact that the process is rather expensive and the obtained layers are relatively thin, the possible application of the method for improving the high temperature corrosion resistance in industrial applications is very limited. However, the method can be used as a research tool, in the frame of screening tests and to gain insights in corrosion mechanisms. In this frame the method is used for example on TiAl- and Ni_3Al-based intermetallic alloys and Cr-based alloys. The latter material is also of interest for fuel cell applications. For this activity a high current ion implanter is available.

2. Thin Layer Activation

The principal basis of Thin Layer Activation (TLA) is the creation of radionuclides in a surface layer to a well defined depth of a selected area, by exposure to a high energy charged particle beam. Various nuclides disintegrate with simultaneous emission of nuclide specific γ-radiation. Any loss of activated material due to a surface degradation process, like wear or corrosion, will result in a decrease in γ-activity of the component. TLA offers various advantages, which include area selectivity (i.e. material loss from a particular region can be monitored), high sensitivity and low total activity, in addition to the possibility for in-situ and on-line monitoring (due to the material penetrating properties of γ-radiation and the speed of measurement) of individual elements. Due to these specific properties, TLA can contribute significantly to the monitoring of surface degradation in both research and industrial applications. This holds certainly for the assessment of highly corrosion or wear resistant materials, such as those obtained by surface treatments. Besides laboratory and industrial wear testing the method is also used at IAM for corrosion testing, the latter including cyclic high temperature corrosion. In this frame the method is used, for example, on Cr based alloys and thermal barrier coatings. For these TLA studies the group possesses a wide range of advanced facilities, the major one a variable energy light ion cyclotron with all related facilities, infrastructure for handling radioactive materials, a gamma spectrometry laboratory and dedicated cyclic oxidation facilities.

3. Scale Growth Mechanisms

Emphasis lays on the use of tracers, such as ^{18}O and ^{15}N, to study scale growth mechanisms. Analyses are performed using SIMS and SNMS in collaboration with external organisations. Material systems under study include TiAl-based intermetallic alloys and Cr-based alloys. Often these studies are combined with ion implantation. To support this activity, a facility is available for tracer experiments with option for thermal cycling and gas analysis using a mass spectrometer.

4. Cyclic Corrosion Testing

Besides screening tests of different materials and coatings, more recently emphasis has been laid on pre-normative cyclic corrosion testing. High temperature corrosion has been particularly void of Codes of Practice and Standards, resulting in an inability to compare results from different organisations, and to many workers repeating the same mistakes and omissions. The activity is focused on investigating the influence of test parameters on the results, with the objective of helping to formulate test guidelines. For this purpose besides classical multi-specimen test facilities, thermobalances for cyclic corrosion testing and TLA facilities are employed.

5. Coatings for Gas Turbine Applications

The work conducted concentrates on the behavior of nickel (X-45, FSX-414) and cobalt (IN738, UD520) base superalloys protected with a range of commercial and novel coating types when exposed to temperatures and atmospheres representative of the first stage of a gas turbine burning a high sulphur, salt free fuel. Coatings include commercial MCrAlY, novel aluminum and aluminum-silicon diffusion coatings and thermal barrier coatings modified with CVD treatments.

Special Equipment

As was indicated in the introduction related to the objectives, emphasis is put on advanced facilities, which are accessible via collaborations to external organisations. Among the specialized facilities, not widely available, are:

1. Variable light ion cyclotron with all related facilities and infrastructure.
2. Gamma spectrometry laboratory.
3. Fully automitized single specimen rigs for cyclic oxidation testing using TLA.
4. Facility for isothermal and cyclic oxidation testing with isotope exchange possibility, e.g. $^{16}O/^{18}O$ with integrated gas analysis (mass spectrometry) facilities.
5. Thermobalances for cyclic oxidation testing under well controlled cyclic conditions.
6. High current ion implanter.
7. Corrosion loops for testing in SO_2 containing gas mixtures.

8. Various surface analytical facilities, including XPS, AES and R.F. powered GD-OES.
9. CVD, PVD and LPPS coating facilities.

Collaboration

Also related to the objectives of the JRC, an active policy is followed to make the capabilities and facilities available to public and private bodies. This might be in the frame of a formal or informal collaboration, research network, work under contract with one or more customers or as partner in a shared cost action under the Framework Programmes of the European Commission, such as e.g. BRITE/EURAM and JOULE. At present the group is involved in all these different types of collaborations.

Future Plans

The mentioned activities dealing with surface degradation studies at the IAM-Ispra site are in rapid expansion. All activities mentioned are expected to be extended further in the future. These are closely related with the activities of the Surface Engineering Unit of IAM-Ispra site. As mentioned, emphasis is and will be put on external collaborations in relation to advanced techniques, which would normally lie outside the scope and capabilities of national organisations and should thus be set up at an European level.

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Scientific Key Words: Bond/thermal barrier coatings; Burner rigs; Ceramics corrosion; Coal-ash corrosion; Coated and uncoated superalloys;Corrosion-mechanical property interactions; Cyclic oxidation; Deposits/heat transfer; Gasification; Heat exchanger materials; Hot corrosion; Intermetallics; ODS alloys; Oxidation/sulfidation; Probes; Reducing environments; Salt deposits; Silicon carbide/ combustion atmosphere; Waste incinerator materials

Technical Key Words: Advanced steam conditions; Atmospheric pressure fluidized-bed combustor; Coal-fired boiler; Condensate (dew-point/downtime) corrosion; Oil-fired boiler; Waste incineration; Very high-temperature heat exchangers; Land-based gas turbines; Thermal barrier coating systems; Coal gasification; Syngas coolers; Heat exchangers

SCOPE OF RESEARCH

Fundamental Approach

The object of the research activity is the evaluation of the corrosion resistance of alloys and coatings for critical components in electric power plants, mainly conventional and advanced combustors and/or boilers, land-based gas turbines, coal gasification and waste-to-energy systems. The emphasis is on the simulation of corrosion damage mechanisms, both devising appropriate laboratory tests and developing probes to allow the exposure of specimens in the service environment. As a consequence, the research includes studies of the combustion gas thermochemistry, the formation of aggressive deposits, the deposit- and/or gaseous species-reaction with the material, the influence of heat flux on the corrosion mechanism and, lastly, the influence of thermal cycling and mechanical damage mechanisms, such as fatigue and creep, on both coating and protective oxide scale integrity. Since the beginning of 1996 the group has been operating a gas/oil-fired combustor that will allow it to perform corrosion tests in a true combustion atmosphere. In the area of in-field exposure, destructive thermal exchanging probes are already available and on-line monitoring probes are under development. Recently, a co-operation has set up with ENEL SpA in the frame of a European project for the standardization of high temperature corrosion testing.

Applications, Engineering Achievement and Technology Transfer

The experimental work is devoted to collecting engineering data on the corrosion behavior of conventional and innovative materials and coatings to allow an estimation of service life on the most critical components in the energy field. Most of the work has been carried out in co-operation with ENEL SpA, the Italian electric power utility, some municipal utilities, materials manufacturers and OEMs.

More recently, some attention has been devoted to the corrosion problems in the Municipal Solid Waste (MSW) incinerators.

Specific Topics

1. Corrosion of Materials for Fossil-Fired Boilers

This research is relevant to the choice of materials for the superheaters of the advanced steam cycles in the fossil-fired thermoelectric power stations. The tests are being carried out on T22, T91, E911, 304SS and 347SS, under heat flux conditions by means of cooled probes inserted in a furnace. Before the exposure to the simulated combustion atmosphere, the specimens are sprayed with alkali sulphates or with sulphate/vanadate salt mixtures. The metal test temperature ranges from 540°C to 650°C. Currently the influence of different amounts of SO_2/SO_3 and HCl is being studied.

2. Corrosion of Materials for Very High Temperature Heat Exchangers

The activity is being performed in the framework of the European COST-501 R.III Program. Tests have been performed at 850 and 1100°C on ODS alloys MA956, PM2000 and ODM 751 in oxidizing gaseous atmosphere on specimens, both as-received and contaminated with sodium sulphate. At the moment, these alloys are being exposed to flue gas in a propane fuelled combustor at 1200°C and daily cycled to room temperature.

3. Corrosion in Reducing Atmospheres

The activity has been performed in the framework of the COST Program. The aim of the work was to assess the corrosion performance of ODS alloys and other commercial alloys (Alloy 800H and Sanicro 28) under Downtime Corrosion condition. The specimens were exposed for up to 1000 h at 500°C and 350°C to a simulated Coal Gasification Atmosphere (CGA), employing gaseous mixtures composed of H_2-CO-H_2S-HCl-H_2O, and cycled to room temperature every 100 h. Following the high temperature period the specimen sheets were mechanically stressed and exposed to moist air up to 720 h, to evaluate the occurrence of pitting and/or SCC.

4. Hot Corrosion of Materials for Land-Based Gas Turbines

The aim of this work was to evaluate the resistance to type-I and -II hot corrosion of Ni- and Co-base superalloys, coatings and thermal barriers employed for blades and vanes in GT. A variety of materials (IN738, IN939, U510, U520, X45, FSX-414), MCrAlY coatings and YPSZ thermal barriers has been tested in the laboratory at 700-900°C, continuously condensing Na_2SO_4 vapours on the specimen surface, according to the 'Dean test' methodology. Some tests in heat-flux condition (T_{gas} = 1300°C) have been performed too. Limited tests were carried out on a TiAl intermetallic alloy. High temperature corrosion/fatigue tests were carried out on IN738 at 850°C, which allowed a LCF life vs. strain curve to be drawn.

5. Corrosion in MSW Incinerator.

This activity has been operated since 1994. Cooled probes are being exposed in the superheater area of some MSW incinerators in northern Italy. Low-alloyed ferritic steels, austenitic stainless steels, co-extruded and laser cladded coatings are under test.

6. High Temperature Oxidation of Monolithic and Ceramic Composites

Type II hot corrosion of SiC joined tubes is being evaluated. Some specimens are exposed to the Dean test at 900°C, while other specimens have been previously coated with a mixture of coal ash and Na_2SO_4 and then thermal aged at 900°C up to 2000 h for evaluating the reduction of mechanical properties. The oxidation kinetics of four ceramic matrix composites are being determinated at 1350°C up to 2000 h, at 4 bar pressure, in CO_2-O_2-H_2O gaseous mixture.

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Scientific Key Words: High temperature water corrosion; Life prediction; Performance/lifetime; Pitting

Technical Key Words: Nuclear power systems

SCOPE OF RESEARCH

All the research activities are focused on the stress-corrosion cracking issue for boiling water reactor (BWR) plant materials. The activities cover all the aspects of the issue, from the mechanistic aspect to the countermeasures, as indicated in the following abstracts.

Specific Topics

1. *Effects of Materials Factors on the Stress Corrosion Cracking Susceptibility of Stainless Alloys in Simulated BWR Primary Coolant Environment*

The effect of grain-boundary chromium depletion has been quantitatively demonstrated for Alloy 600 family alloys as well as stainless steels. A parameter, called the stress corrosion resistivity index (SCRI), that assesses the relative resistance of a material to stress corrosion cracking on the basis of the alloy chemistry has been proposed for Alloy 600 family alloys. Other sensitization mechanisms than the chromium depletion, including the grain boundary segregation of impurity elements, are being investigated for the abave mentioned alloys.

2. *Effects of Environmental Factors on the Stress-Corrosion Cracking Susceptibility of BWR Plant Materials*

The effects of electrode potential and solution impurities on the stress corrosion cracking susceptibility of carbon/low alloy steels, stainless steels, and Ni-base alloys are being investigated by means of the slow strain rate test and the creviced bent beam test. This work is partly supported by the Tokyo Electric Power Co.

3. *Predictive Modeling for the Stress Corrosion Cracking Life*

A predictive model for the initiation time of the stress corrosion cracking is being developed for the BWR plant materials, based on detailed observation for the crack initiation process and mechanistic consideration. This work is partly supported by the Tokyo Electric Power Co.

4. *Development of the Electrochemical Noise Analysis Technique for Monitoring the Stress Corrosion Crack Initiation Process*

The free corrosion potential fluctuation behavior is being detailed for the development of the monitoring technique for the stress corrosion crack initiation.

5. *Photoelectrochemical Protection of Stainless Alloys from the Stress Corrosion Cracking*

A noble cathodic protection method using the photoelectrochemical reaction taking place on the titanium dioxide semiconductor, placed onto the surface of BWR plant material, is being developed. This work is partly supported by the Tokyo Electric Power Co.

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Technical Key Words: Catalyst support systems; Heating elements; Industrial furnaces; Fluidized-bed combustor

SCOPE OF RESEARCH

Fundamental Approach

The aim of the research is to investigate mechanisms of high temperature oxidation and high temperature corrosion of heat resistant alloys in detail and to give fundamental information to development of new materials and to offer new knowledge to the next generation. The research includes fundamental studies such as sulfur effects of heat resistant alloys with different sulfur contents, coatings of reactive element oxides (Al_2O_3, SiO_2, Y_2O_3, CeO_2) and ion implantation of reactive element (Y) to heat resistant alloys, additions of reactive elements (Y, La, Gd, Ho, Er, Ti, Zr, Hf) to heat resistant alloys, growth processes and spalling of oxide on the heat resistant alloys. Extensive programs have included in cyclic and isothermal oxidation, and in in-situ observation during oxidation.

Specific Topics

1. Sulfur Influence on High Temperature Oxidation of Heat Resistant Alloys

This research is being carried out into the influence of sulfur on Fe-20Cr-4Al and Ni-20Cr-1Si alloys with different sulfur contents. Emphasis is being placed on the influence of sulfur concerning the growth mechanism of the oxide, oxide morphology, the spalling process of oxide and the behavior of chromium sulfide in cyclic and isothermal oxidation, and in-situ observation of oxidation.

2. Coatings of Reactive Element Oxides and Ion Implantation of Reactive Element to Heat Resistant Alloys

This work is being carried out into the improvement of oxidation resistance by coatings of reactive element oxides (Al_2O_3, SiO_2, Y_2O_3, CeO_2) and ion implantation of reactive element (Y) to Ni-20Cr-1Si alloys. A detailed study is being carried out into the influence of different reactive element oxides and of ion implantation of the reactive element, phase transformation of SiO_2, oxide grain size and oxide composition on the alloys.

3. The Influence of Reactive Elements to Heat Resistant Alloys

This research is being carried out into the influence of additions of reactive elements (Y, La, Pr, Gd, Ho, Er, Ti, Zr, Hf) to Fe-20Cr-4Al and Ni-20Cr-1Si alloys. Emphasis is being placed on the influence of chemical and physical properties of added elements such as atomic radius, ion radius, free energy of formation of oxide, distribution of intermetallic compounds and reactive elements.

4. Corrosion Behavior of Heat Resistant Alloys

This work is supported by the Grant-in Aid on Priority Areas, Ministry of Education, Japan. The overall aim of the work is to develop candidate advanced corrosion resistant materials for the development of thermochemical hydrogen production process UT-3 using cycle reactions Ca-Br-Fe system.

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Scientific Key Words: Oxidation; Passivation; Internal oxidation

Technical Key Words: Stainless steel; Hot strip; Heating furnace

SCOPE OF RESEARCH

Fundamental Approach

An effect of the passive film on high temperature oxidation behavior of ferritic stainless steels, 17Cr-1.2Mo-0.3Ti and 16-19 Cr ferritic stainless steels containing up to 2 wt% Mo, has been studied at 1000°C and 1050°C in air. The main results were as follows:

1. The longer the time from the polishing of the specimens to the start of the oxidation tests, the better the oxidation resistance of 17Cr-1.2Mo-0.3Ti steel.

2. At the initial stage of high temperature oxidation, Cr_2O_3 scale was observed on the specimen that was oxidized after a long period of exposure in air at room temperature. On the other hand, the specimen that was oxidized immediately after polishing developed $(Cr, Mn)_3O_4$ scales.

3. Cr concentration in the passive film increased with time elapsed after polishing.

4. Mo addition to ferritic stainless steels promoted the formation of Cr_2O_3 at the early stage of oxidation, improving their oxidation resistance.

5. The passive film became thinner but probably more dense with increasing Mo content.

Currently, the high temperature oxidation behavior of stainless steel slab entering the heating furnace for hot rolling, and the secondary internal oxidation behavior on hot strip coil during cooling to room temperature, are being investigated. In the near future hot corrosion behavior of heat resistant alloys is to be studied in order to develop new materials for a superheater tube to be put in a municipal incinerator.

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Scientific Key Words: Hot corrosion; Molten salts; Electrochemical measurement; Oxidation/choridation; Coating methods

Technical Key Words: Waste-fired boiler; Future gas turbine materials

SCOPE OF RESEARCH

Specific Topics

1. Electrochemical Study of Hot Corrosion of Metals in Molten Salt

This research is being undertaken in order to clarify the hot corrosion mechanism of Ni-base superalloys and various pure metals constituting the superalloys in molten Na_2SO_4, NaCl, Na_2SO_4-NaCl mixture, $NaCO_3$ and $NaNO_3$ at high temperature.

2. Formation of High Corrosion-Resistant Surface Layer by Electrodeposition Using Molten Salt

Electrodeposition using molten salt is advantageous to the formation of refractory metals and rare earth metals. This work is being carried out with a view to obtaining a newly high corrosion-resistant surface layer by the electrodeposition of refractory metals and rare earth metals using molten salts.

3. High-Temperature Oxidation of Metals in Oxygen Atmosphere Containing a Small Amount of Hydrogen Chloride

The aim of this research is to undertake a fundamental study of the oxidation of various metals and alloys in waste incinerator atmospheres. Emphasis is being placed on the effect of a small amount of hydrogen chloride on the oxidation of the metals.

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Scientific Key Words:	Alumina; Amorphous alloys; Coatings; Oxidation/sulfidation; Refractory alloys; Sputter deposition; Sulfidation resistance/refractory metals
Technical Key Words:	Coal-fired boiler; Waste-fired boiler; Coal gasification; Petrochemical industry

SCOPE OF RESEARCH

Fundamental Approach

The main objective of the research is to understand the oxidation and sulfidation behavior of novel Al-refractory metal and Cr-refractory metal alloys in order to tailor new materials or coatings, resistant against both sulfidation and oxidation at high temperatures. The materials are prepared mostly by using a sputter deposition technique, which is suited for preparing single phase metastable alloys in a wide composition range, even if the melting point of one of alloying constituents far exceeds the boiling point of the other constituents. Relatively simple alloy systems, containing only elements which form protective oxide scales, such as aluminium, chromium and silicon, and refractory metals which form protective sulfide scales, have been examined. The research includes fundamental studies of the effect of alloying elements on the protective properties and growth mechanism of oxide and sulfide scales. The problems of sputter-deposited sulfidation- and oxidation-resistant alloy coatings on practical materials have also been examined. The research is collaborative with Mrowec, S., Prof., of the Group in the Department of Solid State Chemistry, University of Mining and Metallurgy, Cracow, Poland. Fundamental studies of oxidation behavior of amorphous alloys, in connection with developing novel catalysts from amorphous alloy precursors, are also one of the important research subjects.

Applications, Engineering Achievements and Technology Transfer

Most of the laboratory's work is aimed to develop novel materials resistant in sulfidizing and oxidizing environments and novel catalysts formed from oxidation of amorphous alloys. The former materials can be used in gasification and liquefaction of coal, the petrochemical industry, waste combustion systems and so on, and the latter would be linked to conservation of the global atmosphere by catalytic decomposition or transformation of pollutant gases.

Specific Topics

1. *Oxidation and Sulfidation Behavior of Sputter-Deposited Al-Refractory Metal Alloys at High Temperatures*

Since no metallic materials resistant in both oxidizing and sulfidizing environments are presently known, this work is being carried out to tailor novel oxidation- and sulfidation-resistant alloys. Single-phase amorphous or solid solution Al-refractory metal alloys have been prepared by sputter deposition, and their oxidation and sulfidation behavior has been examined. Some alloys, such as Al-Mo, Al-Mo-Si and Al-Nb-Si alloys, possess extremely high sulfidation resistance, better than the corresponding refractory metals and high oxidation resistance comparable to the typical chromia-forming alloys.

2. *Oxidation and Sulfidation Behavior of Sputter-Deposited Cr-Refractory Metal Alloys at High Temperatures*

As well as Al-refractory metal alloys, the oxidation and sulfidation behavior of sputter-deposited amorphous or solid solution Cr-refractory metal alloys have been examined. These alloys are resistant in sulfidizing environments at high temperatures, being comparable to the corresponding refractory metal alloys, due to the formation of a refractory metal sulfide layer as an inner layer of the scale. The chromium-rich Cr-Nb and Cr-Ta alloys also shows high oxidation resistance.

3. *Oxidation Behavior of Amorphous Alloy Precursors of Catalysts*

In connection with development of novel catalysts, prepared by oxidation of amorphous alloys, for decomposition or transformation of pollutant gases, such as NO, chlorofluorocarbons and carbon dioxide, a fundamental study of the oxidation of such alloys have been carried out. Characterization of the oxides has been performed using transmission electron microscopy, scanning electron microscopy, physical and chemical gas adsorption methods etc.

RECENT PUBLICATIONS

1. High Temperature Oxidation and Sulfidation of Al-Refractory Metal Alloys

1. Habazaki, H., Dabek, J., Hashimoto, K., Mrowec, S. and Danielewski M., "High Temperature Corrosion Behavior of Some Al-Mo and Al-Mo-Si Alloys," Corrosion, Electrochemistry and Catalysis of Metastable Metals and Intermetallics, Eds. C.R. Clayton and K. Hashimoto, The Electrochemical Society, pp224-235 (1993).

2. Habazaki, H., Dabek, J., Hashimoto, K., Mrowec, S. and Danielewski, M., "Oxidation Behaviour of Sputter-Deposited Amorphous Al-Mo Alloys at High Temperatures," Proc. 10th European Corrosion Congress (1993).

3. Hashimoto, K., Kumagai, N., Yoshioka, H., Kim, J.H, Akiyama, E., Habazaki, H., Mrowec, S., Kawashima, A. and Asami, K., "Corrosion-Resistant Amorphous Surface Alloys," Corrosion Science, 35, 363-370 (1993).

4. Habazaki, H., Dabek, J., Hashimoto, K., Mrowec, S. and Danielewski, M., "The Sulphidation and Oxidation Behaviour of Sputter-Deposited Amorphous Al-Mo Alloys at High Temperatures," Corrosion Science, 34, 183-200 (1994).

5. Habazaki, H., Takahiro, K., Yamaguchi, S., Hashimoto, K., Dabek, J., Mrowec, S. and Danielewski, M., "On the Growth Mechanism of the Sulphide Scale on Amorphous Al-Mo Alloys," Corrosion Science, 36, 199-202 (1994).

6. Habazaki, H., Hashimoto, K. and Mrowec, S., "Corrosion-Resistant Amorphous Alloys at High Temperatures," Bouseikanri, 7-12 (1994).

7. Habazaki, H., Takahiro, K., Yamaguchi, S., Hashimoto, K., Dabek, J., Mrowec, S. and Danielewski, M., "New Amorphous Alloys Resistant to High Temperature Corrosion," Materials Science and Engineering, A181/A182, 1099-1103 (1994).

8. Grzesik, Z., Habazaki, H., Hashimoto, K. and Mrowec, S., "The Sulphidation Behavior of Mo-Al Alloys with Low Aluminum Contents," Corrosion Science, 36, 1499-1511 (1994).

9. Mitsui, H., Habazaki, H., Hashimoto, K. and Mrowec, S., "High Temperature Corrosion of Sputter-Deposited Al-Nb Alloys," Transaction of Material Research Society Japan, 14A, 243-246 (1994).

10. Habazaki, H., Mitsui, H., Asami, K., Mrowec, S. and Hashimoto, K., "Sputter-Deposited Amorphous Al-Mo-Si Alloys Resistant to High Temperature Sulfidation

and Oxidation," Transactions of the Materials Research Society ofJapan, 14A, 309-312 (1994).

11. Habazaki, H., Grzesik, Z., Takahiro, K., Yamaguchi, S., Hashimoto, K., Dabek, J., Danielewski, M. and Mrowec, S., "Protective Oxide and Sulfide Films on Sputter-Deposited Amorphous Al-Mo and Al-Mo-Si Alloys at High Temperatures," Proc. 7th Int. Symposium on Oxide Films on Metals and Alloys, Eds. K. R. Hebert and G. E. Thompson, The Electrochemical Society, Pennington, pp176-187 (1994).

12. Grzesik, Z., Takahiro, K., Yamaguchi, S., Hashimoto, K. and Mrowec, S., "An RBS Study of the Sulphidation Behaviour of Niobium and Nb-Al Alloys," Corrosion Science, 37, 801-810 (1995).

13. Grzesik, Z., Mitsui, H., Asami, K., Hashimoto K. and Mrowec, S., "The Sulphidation of Sputter-Deposited Niobium-Base Aluminium Alloys," Corrosion Science, 37, 1045-1058 (1995).

14. Habazaki, H., Hashimoto, K., Mrowec, S. and Danielewski, M., "Novel Al-Mo and Al-Mo-Si Alloys Resistant to Sulfidizing and Oxidizing Environments," Zairyo to Kankyo (Corrosion Engineering), 44, 174-182 (1995).

15. Hashimoto, K., Park, P.-Y., Kim, J.-H., Yoshioka, H., Akiyama, E., Habazaki, H., Kawashima, A., Asami, K., Grzesik, Z. and Mrowec, S., "Recent Progress in Corrosion-Resistant Metastable Alloys," Materials Science and Engineering, A198, 1-10 (1995).

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20. Lee, D.B., Mitsui, H., Habazaki, H., Kawashima, A. and Hashimoto, K., "The High Temperature Sulfidation Behavior of Nb-Al-Si Coatings Sputter-Deposited on a Stainless Steel," Corrosion Science, 38, 2031-2042 (1996).

2. High Temperature Oxidation of Amorphous Zirconium Alloys

21. Asami, K., Kimura, H.M., Inoue, A., Hashimoto, K. and Masumoto, T., "Oxidation Behavior of Amorphous Zr-Ni Alloys in Air," Corrosion, Electrochemistry and Catalysis of Metastable Metals and Intermetallics, Eds. C.R. Clayton and K. Hashimoto, The Electrochemical Society, pp236-245 (1993).

22. Asami, K., Kimura, H.M., Hashimoto, K. and Masumoto, T., "High Temperature Oxidation Behavior of Amorphous Zr-Ni Alloys in Air," Materials Transactions, JIM, 36, 988-994 (1995).

3. Patents

23. Hashimoto, K, Habazaki, H., Mrowec, S. and Danielewski, M., "Amorphous Alloys Resistant Against Hot Corrosion," Japan Application No. 92-85529 & 92-85530.

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Scientific Key Words: Alumina growth; Cyclic oxidation; Heat-resistant steels; Reactive element effect; Transmission electron microscopy; Stainless steels

Technical Key Words: Emissions control equipment

SCOPE OF RESEARCH

Oxidation behavior of stainless steels is being investigated to apply them for high temperature environments.

RECENT PUBLICATIONS

1. High-Temperature Oxidation

1. Kawasaki, T. and Ishii, K., "Development of Oxidation Resistant Fe-20Cr-5Al Alloy Foil for Automobile Catalytic Converter Use," Proceedings of International Conference on Stainless Steels, Chiba ISIJ, 1205-1211 (1991).

2. Ishii, K. and Kawasaki, T., "Effect of Lanthanum or Cerium Addition on High Temperature Oxidation Resistance of Fe-Cr-Al Alloy Foils," Journal of the Institute of Materials, 56, 854-862 (1992).

3. Okabe, S., Kohno, M., Ishii, K., Yukomoto, M. and Nozaki, T., "Oxidation Resistance of Rapidly Solidified Fe-Cr-Al Ribbons at High Temperature," Materials Science and Engineering, A181/A182, 1104-1108 (1994).

4. Ishii, K., Kohno, M., Ishikawa, S. and Satoh, S., "Effect of Rare-Earth Elements on High-Temperature Oxidation Resistance of Fe-20Cr-5Al Alloy Foils," Trans. JIM, 38, 787-792 (1997)

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Scientific Key Words: Coal-ash corrosion; Creep/corrosion interactions; Electrochemical measurements; Erosion-corrosion; Hot corrosion; Life assessment; Mixed gases; Molten salts; Oxidation/sulfidation, plasma coatings; Steam-side corrosion; X-ray photoelectron spectroscopy

Technical Key Words: Advanced steam conditions; Boiler tube failures; Coal-fired boiler; Furnace wall corrosion; Gas turbines; Waste incineration; Pressurized fluidized-bed combustor; Molten carbonate fuel cells; Coal gasification

SCOPE OF RESEARCH

Most of the research activity is undertaken to support the developments of new energy processes, like the advanced steam cycle boiler, the pressurized fluidized-bed boiler, the molten carbonate fuel cell, coal gasification plant and the high efficiency waste incinerator. Also, trouble shooting in conventional plants, like waterwall corrosion of fossil fuel-fired boilers and hot corrosion in gas turbines, is undertaken.

Recent principal subjects are as follows:

Specific Topics

1. Materials for Coal Gasification

- Development of an alloy for the superheater tube of a syngas cooler, which has excellent resistance against high-temperature sulfidation and pitting corrosion during shutdown (downtime corrosion) - collaboration with Tokyo Electric Co and Sumitomo Metals Co.

- Corrosion test of candidate materials for superheater tubes in 6 ton/day pilot IGCC plant.
- Corrosion measurement of an evaporator tube (T-11) of a syngas cooler in 6 ton/day IGCC pilot plant.

2. New Ferritic Steel for Advanced Steam Cycle Boiler

- Evaluation of the resistance of a new high strength 9-12Cr steels for fire-side and steam side corrosion.
- Study of effects of Mo, W and V additions in low alloy steels on the corrosion resistance in steam and air at high temperatures.

3. Corrosion in Fossil-Fired Boilers

- Effect of HCl on the corrosion of waterwall tubes and superheater tubes.
- Corrosion behavior of the waterwall tubes under substoichiometric combustion (high temperature sulfidation).
- Probe test of candidate materials of superheater tubes in an Orimulsion fired actual boiler.

4. Incinerator

- Development of a new material of superheater tube for a high efficiency incinerator - NEDO project.
- Evaluation of the corrosion resistance of candidate materials for superheater tubes in a high efficiency pilot plant (steam conditions: 500°C, 100 atm).
- Effect of HCl on the corrosion of waterwall and superheater tubes
- Effect of heavy metals (Zn, Pb) in the ash on the corrosion of waterwall tubes and superheater tubes.
- Effect of stress on the intergranular corrosion of heat transfer tubes.

5. Molten Carbonate Fuel Cell (MCFC)

- Development of a new material for the center plate between electrolyte and electrode.
- Effect of Mo and Nb on the corrosion in a molten carbonate.
- Evaluation for the corrosion resistance of cathode current collector (AISI 316L) in Li_2Co_3-Na_2CO_3 molten salt.

- Effect of H_2 permeation on the corrosion of a center plate for the cathode side.
- Evaluation of long-term corrosion resistance of an aluminized wet seal material.
- Effect of the basaicity of a carbonate melt on the solubility of various oxides.

6. Erosion and Spray Coating

- Effect of spray conditions on the erosion resistance of ceramic coatings.
- Evaluation of erosion resistance of heat transfer tubes in a pressurized fluidized bed.
- Effect of gas atmosphere on erosion at high temperatures.

RECENT PUBLICATIONS

1. Coal Gasification

1. Kihara, S., Nakagawa, K. and Saito, K., "Effect of Gas Composition and Pressure on High Temperature Corrosion of Various Steels in Coal Gasification Atmospheres," Materials at High Temperature, 11, 65-69 (1993).

2. Kihara, S., Matsumoto, S., Saito, K. and Ogawa, H., "Development of Dual-Wall Tube for a Coal Gasification Plant Through a Hot Isostatic Pressing - Hit Extrusion Process," Materials at High Temperature, 11, 65-69 (1993).

3. Sawaragi, Y., Otsuka, N., Kihara, S. and Bakker, W.T., "A New Austenitic Alloy Containing 3.5% Vanadium Resistant to Coal Gasfire Corrosion Environment," Materials at High Temperature, 11, 176-180 (1993).

4. Kihara, S., "Corrosion of T-11 Syngas Cooler Tubes in IGCC Pilot Plant," Presented at 2nd International Workshop on Corrosion in Advanced Power Plants, EPRI, Wyndham Harbour Island, Fl, March 3-6 (1997).

2. Waterwall Corrosion

5. Nakagawa, K., Kitagawa, M. and Tsumita, Y., "High Temperature Corrosion of Waterwall Tubes in Coal-Fired Combustion Gases," Journal de Physique 4 Colloque C9, Supplement au Journal de Physique 3, 3, 787-796 (1993).

3. Incinerator

6. Nakagawa, K. and Isozaki, T., "Fireside Corrosion in Reducing Waste Incineration Environments, CORROSION/94, Paper No. 177 (1994).

7. Otsuka, N., Nakagawa, K., Kawahara, Y., Tukaue, Y., Yamamoto, A. and Yukawa, K., "An Evaluation of Corrosion Resistant Alloys by Laboratory Corrosion Test," CORROSION/95, Paper No. 565 (1995).

8. Nakagawa, K. and Matsunaga, Y., "An Electrochemical Investigation of Corrosion of Superheater Tube in Waste Incineration Environment," CORROSION/97, Paper No. 164 (1997).

9. Matsunaga, Y. and Nakagawa, K., "Corrosion Loss Measurement of Boiler Tubes in Waste Incineration Environment," CORROSION/97, Paper No. 163 (1997).

4. MCFC

10. Matsumoto, K. and Nakagawa, K., "Influence of Carbon Dioxide on Corrosion Behavior of Stainless Steel in Molten Lithium-Sodium Carbonate," ECS 190th Meeting, No. 734 (1996).

5. Spray Coating

11. Sonoya, K., Tomisawa, Y., Kitagawa, M. and Kajigaya, I., "Low Cycle Failure Life of Ceramic Sprayed Cr-Mo Steel," Journal of Materials Science Society, 42, 1077-1082 (1993).

12. Sonoya, K., "Fatigue Strength of Ceramic-Coated Steel at Elevated Temperature," Proceedings of the 9th National Thermal Spray Conference, Cincinnati, Ohio, Oct. 7-11 (1996).

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Scientific Key Words: Oxidation; Thermodynamics in oxide; Diffusion; Reactive element effect

Technical Key Words: Molybdenum silicide; Solid oxide fuel cells

SCOPE OF RESEARCH

High temperature oxidation of metals, alloys and intermetallics is a solid state electrochemical process involving metal oxides. The better understanding of the process requires the knowledge of thermodynamic and transport properties of metals and oxides concerned. The Gibbs energy of formation and defect structure of oxides and diffusivity of constituent elements in oxides have been measured. Our current interests are focused on the reactive element effect, oxidation of intermetallics and application of alloys to solid oxide fuel cells.

Specific Topics

1. Thermodynamics and Transport Properties of Rare Earth Chromite ($LaCrO_3$)

Gibbs energy of formation of $YCrO_3$ and diffusivity of Y ion have been determined. Diffusivity measurement of La in $LaCrO_3$ is now going on.

2. High Temperature Oxidation of Intermetallics

High temperature oxidation of $MoSi_2$-based intermetallics (Mo-Si-X) has been carried out at temperature up to 2000K. This research was supported by Ministry of Education, Culture and Sports, Japan (MECS) and has been continued partly as a co-operation of Japan Ultrahigh Temperature Material. Dip formation of $Mo(Si, Al)_2$ and $Nb(Si,Al)_2$

using molten Al-Si is in progress for application of anti-oxidation coating. This project is also supported by MECS. High temperature oxidation of Nb-Al intermetallics has started as a co-operative work with Gifu Prefectural Metal Research Institute.

3. Application of Chromia-Forming Alloys to Interconnector in Solid Oxide Fuel Cell

Research on application of Ni-Cr alloys coated with porous (La,Sr)CoO_3 to an interconnector of SOFC operated at 1273K was conducted as a co-operative work with NKK Co. Similar work of Fe-Cr ferritic alloys for SOFC operated at 1073K has started as a research project of the Japan Petroleum Institute commissioned by the Petroleum Energy Center with subsidy by the Ministry of International Trade and Industry (MITI), Japan.

RECENT PUBLICATIONS

1. Thermodynamics and Transport Properties of Rare Earth Chromite ($LnCrO_3$)

1. Kawamura, K., Maruyama, T. and Nagata, K., "The Equilibrium Oxygen Pressure Over the Cr-Y_2O_3-$YCrO_3$ Coexistence Measured with the Galvanic Cell Using Stabilized ZrO_2 Solid Electrolyte," Metallurgy and Materials Transactions B, 26B, 289-294 (1995).

2. Kawamura, K., Saiki, A., Maruyama, T. and Nagata, K., "Diffusion Coefficient of Yttrium Ion in $YCrO_3$," Journal of the Electrochemical Society, 142, 3073-3077 (1995).

3. Akashi, T., Nanko, M., Maruyama, T., Shiraishi, Y. and Tanabe, J., "Diffusion Coefficient of La^{3+} in $LaCrO_3$ Determined by Solid State Reaction," Proc. Of the 5th International Symposium on Solid Oxide Fuel Cells, Aachen, The Electrochemical Society, 1263-1272 (1997).

2. High Temperature Oxidation of Intermetallics

4. Maruyama, T., Yanagihara, K. and Nagata, K., "High Temperature Oxidation of Intermetallic Compounds of $Mo(Si_{1-x},Al_x)_2$," Corrosion Science, 35, 939-944 (1993).

5. Saito, Y., Onay, B. and Maruyama, T., "The Reactive Element Effect (REE) in Oxidation of Alloys," Journal de Physique, IV, 3, 217-230 (1993).

6. Yanagihara, K., Maruyama, T. and Nagata, K., "Isothermal and Cyclic Oxidation of $Mo(Si_{1-x},Al_x)_2$ up to 2048K," Materials Transactions JIM, 34, 1200-1206 (1993).

7. Yanagihara, K., Maruyama, T. and Nagata, K., "Dip-Coating of $Mo(Si,Al)_2$ on Mo with an Al-Si Melt," Tetsu-to-Hagane, 80, 90-94 (Japanese) (1994).

8. Yanagihara, K., Maruyama, T. and Nagata, K., "High Temperature Oxidation of Mo-Si-X Intermetallics (X=Al, Ti, Ta, Zr and Y)," Intermetallics, 3, 243-251 (1995).

9. Yanagihara, K., Maruyama, T. and Nagata, K., "Effect of Third Elements on the Pesting Suppression of Mo-Si-X Intermetallics (X=Al, Ti, Ta, Zr and Y)," Intermetallics, 4, S133-S139 (1996).

10. Yanagihara, K., Przyblyski, K. and Maruyama, T., "The Role of Microstructure on Pesting During Oxidation of $MoSi_2$ and $Mo(Si,Al)_2$ at 773K," Oxidation of Metals, 47, 277-293 (1997).

3. Application of Chromia-Forming Alloys to Interconnector in Solid Oxide Fuel Cell

11. Kadowaki, T., Shiomitsu, T., Matsuda, E., Nakagawa, H., Tsuneizumi, H. and Maruyama T., "Applicability of Heat Resisting Alloys to the Separator of Planner Type Solid Oxide Fuel Cell," Solid State Ionics, 67, 65-69 (1993).

12. Shiomitsu, T., Kadowaki, T., Ogawa, T. and Maruyama, T., "The Influence of $(La,Sr)CoO_3$ Coatings on the Electrical Resistance of Ni-20Cr Alloys in High Temperature Oxidizing Atmosphere," Proc. of the 4^{th} International Symposium on Solid Oxide Fuel Cells, Yokohama, The Electrochemical Society, 850-857 (1995).

13. Maruyama, T., Inoue, T. and Nagata, K., "Electrical Conductivity of $SrCrO_4$ and $Sr_3Cr_2O_8$ at Elevated Temperatures in Relation to the Highly Conductive Chromia Scale Formed on an Alloy Separator in SOFC," Proc. of the 4^{th} International Symposium on Solid Oxide Fuel Cells, Yokohama, The Electrochemical Society, 889-894 (1995).

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Scientific Key Words: Dynamic in-situ study; ODS alloys; Surface reactions; Initial oxidation; Photoelectron emission; Atomic force microscopy; I-V property of oxide

SCOPE OF RESEARCH

Fundamental Approach

Spalling of the protective film is fatal to high-temperature alloys. Factors which control the spalling have been studied by measuring the surface segregation with Auger electron spectroscopy. The effect of dispersed alloys on spalling of coating film was studied. The initial oxidation behavior of alloys has not been studied too much because of difficulty of measurement. To estimate the long-term, high-temperature property by the initial oxidation behavior, the relationship between the initial oxidation behavior and long-term oxidation behavior is being studied by atomic force microscopy (AFM) and photoelectron emission measurement.

Applications, Engineering Achievements and Technology Transfer

Specific Topics

1. The Effect of Dispersed Alloys on Spalling of Coating Film

Cyclic oxidation tests and measurements of surface segregation of S on several alloys have been made and it was found that the degree of oxide scale spalling increased with increasing surface segregation rate of S. Thus it has been concluded that interfacial segregation of S promotes scale spalling, and that rare earth metals (REM) suppress the spalling through trapping S as a sulfide. The S effect was also found on coating films. The effect of dispersed alloys on spalling of coating films was studied.

2. The Effect of Initial Oxidation Behavior on Oxidation Resistance of Alloys

An in-situ, photoelectron emission measurement system has been developed at high temperature. By using this system, the surface cleaning process and the nucleation of oxide for various alloys can be estimated. The initial stage of oxidation has also been studied by an atomic force microscope (AFM), combining the photoelectron emission measurement. The nucleation and the growth process of oxide was observed by AFM. The I-V curve property change of oxide with the progress of oxidation was also studied by AFM.

RECENT PUBLICATIONS

1. Ikeda, Y., Sumiyoshi, H., Matsuoka, S. and Takeuchi, E., "Performance of Oxide Coating Films on ODS Alloys," Proceedings of the 2nd International Conference on Structural Application of Mechanical Alloying, Vancouver, September, ASTM International, 125-129 (1993).

2. Washizu, N., Ikeda, Y. and Masuda, H., "Photoelectron Emission During Initial Oxidation at Elevated Temperature of Fe-Cr Alloys in Air," Journal of the Japanese Institute of Metals, 57 (1993).

3. Ikeda, Y., Sumiyoshi, H. and Ishiwata, Y., "Spalling of Al_2O_3 Coating Film on Alloys Doped with Different Oxide for Rare Earth Metal," ISIJ International, 35, 1109-1114 (1995).

4. Mauda, H., Ikeda, Y., Sumiyoshi, H. and Washizu, N., "In-Situ Measurement of Photoelectron Emission During Initial Stage of Oxidation at Elevated Temperature," Journal of the Japanese Institute of Metals, 59 (1995).

5. Sumiyoshi, H. and Ikeda, Y., "Oxidation Property of Y_2O_3 Dispersed Fe-20 mass% Cr Alloys," Journal of the Japanese Institute of Metals, 60, 457-462 (1996).

6. Masuda, H., "SPM Observation of Initial Oxidation at Elevated Temperature," Ceramics, 31 (1996).

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Scientific Key Words: Gasification; Heat exchanger materials; Mixed oxidants with water vapor; Chlorine; Surface modification

Technical Key Words: Coal gasification; Syngas coolers

SCOPE OF RESEARCH

Fundamental Approach

The main objective of current research is to obtain a detailed understanding of the corrosion mechanisms of metallic materials under environmental conditions pertaining to the syngas cooler of a coal gasification system. Studies conducted in this area within the last decade by different groups contributed significantly to the understanding of metal/alloy corrosion in carbon-rich, sulfur-containing gas mixtures at elevated temperatures. As several demonstration or commercial gasification plants are coming-on-line around the world, further work in this area is required due to (a) the planned use of coal with widely different amounts of sulfur and chlorine, (b) the development of gasification processes with varying degrees of water vapor content, and (c) increasing application of new alloys such as 9Cr and 12Cr steels as heat-exchanger materials in steam generation equipment. In the present work, high temperature corrosion behavior of both new and traditional alloys is being investigated with respect to (i)-sulfur and chlorine potentials of the environment, (ii)-water vapor content of the mixed gas, (iii)-chromium content of the alloy, (iv)-total gas pressure and (v)-temperature. Understanding the effect of alloy surface preparation on the morphology and composition of the corrosion products formed in mixed gas environments containing chlorine gas and water vapor is also being targeted in this program.

Applications, Engineering Achievements and Technology Transfer

The current research work is part of a coal-gasification-development-program which was funded, until recently, by the New Energy Development Organization (NEDO) of Japan. During this program, a 50 ton/day-capacity gasification pilot-plant was designed, constructed and operated by the program participants. To demonstrate the developed technology, a gasification plant with 150 ton/day-capacity is being designed by Babcock-Hitachi K.K. and funded, mainly, by the Ministry of Industry and Trade (MITI) of Japan. Besides contributing to the fundamental understanding of high temperature metal corrosion in mixed gas environments, the present work is aimed to provide both qualitative and quantitative materials corrosion data during the design and operational stages of the planned gasification plant.

Specific Topics

1. Corrosion Behavior of Heat Exchanger Tube Materials in Simulated Coal Gasification Environment

Samples of conventional and recently developed Fe-base alloys, which are used as heat exchanger materials in boilers, are exposed to H_2-CO-CO_2-H_2S-HCl-H_2O gas mixtures at 300, 450 and 600°C for up to 2000 hr in both atmospheric and high pressure (30 atg) reaction chambers. In the atmospheric pressure chamber, multi-temperature tests can be conducted simultaneously. 100 hr-long tests conducted on 2.25Cr-1Mo steel samples under a gas mixture of 0.1%H_2S, 0%HCl and 3%H_2O showed that (a) the estimated metal recession rates (mm/y) for 300, 450 and 600°C were 0.31, 1.7 and 9.1, respectively, (b) the main corrosion product was an outer FeS layer at all temperatures and total gas pressures, (c) the development of the subsurface corrosion layer increased with temperature with FeS, Fe_3O_4 and Fe_xC present in this layer at 600°C, (d) the change in total gas pressure did not significantly affect metal recession rates but promoted the formation of carbon-rich iron carbides in the subsurface layer. Currently, 500 hr-long tests are conducted in mixed gas environments containing 0.3% H_2S, 0.035% HCl and varying amounts of water vapor (0-20%).

2. Corrosion Behavior of Some Fe-base Alloys in H_2-H_2O and H_2-H_2O-HCl Gas Mixtures at 700°C

In this study, SUS 310S, 752Z ($\alpha+\gamma$ phase with 5% Al) and MA 956 alloy samples were exposed to H_2-H_2O and H_2-H_2O-HCl gas mixtures with very low partial pressures of oxygen and chlorine gases representing, partially, the environment in the syngas cooler section of a coal gasification plant. Test samples were prepared by one of the following methods; SiC paper-grinding, diamond-paste polishing, shot-peening or electropolishing to investigate the effect of surface condition on the morphology and composition of the corrosion products formed in HCl gas-containing environments.

After 100 hr-long tests the following observations were made; (a) diamond-paste and electropolished samples of the 310S and 752Z alloys had $FeCr_2O_4$-rich product scales while SiC paper-ground and shot-peened samples developed Cr_2O_3-rich scales, (b) addition of HCl gas into the environment increased the amount of spinel phase formed on these two alloy samples regardless of surface preparation, (c) scale adhesion to the MA956 alloy was worse for the diamond-paste and electropolished samples tested in HCl gas-containing gas mixtures. Currently, the effect of surface preparation on HCl-induced high temperature corrosion is being investigated in simulated coal gasification environment for longer test duration.

3. *Testing and Development of Corrosion Resistant Structural Materials for a Coal Gasification Pilot Plant*

This project aimed to develop structural materials for different sections of a coal gasification plant by assessing their corrosion properties through testing in both the laboratory and the pilot plant. The materials studied in this work included 80%Cr_2O_3 and 80-90%$MgCr_2O_4$ ceramics for refractories, Ir metal for thermowells and slag-tap-cover in the gasifier chamber, and metallic alloys for the syngas cooler heat-exchanger tubes. Several different degradation mechanisms were identified for these materials depending on the environmental conditions. These included (a) iron-bursting and erosion for the ceramics due to turbulent gas/slag flow conditions in the gasification chamber, (b) formation of Fe-Ir layers with lower melting temperatures over Ir substrates upon diffusion of Fe from the slag, (c) low-temperature (wet) corrosion of metallic heat-exchanger materials which occurred during downtime of the gasification plant.

RECENT PUBLICATIONS

1. *High Temperature Degradation in Aggressive Gases*

1. Morimoto, T., Önay, B., Fukuda, Y., Kida, E. and Nomura, K., "Materials Exposure Test in the Heat Recovery Boiler of HYCOL Coal Gasification Pilot Plant," Proc. of 2nd Int. Conf. on Heat-Resistant Mats., Eds. K. Natesan, P. Ganesan and G. Lai, ASM Int., Materials Park, USA, 333-339 (1995).

2. Morimoto, T., Matsuoka, T. and Nomura, K., "Materials Experiences for Gasifier Thermowells in the Pilot HYCOL," Materials at High Temperature, 11, (No. 1-4), 118-123 (1993).

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Scientific Key Words: Mixed gases; Oxidation/sulfidation

Technical Key Words: Pressure vessel alloys

SCOPE OF RESEARCH

Polythionic acid stress corrosion cracking could occur to stainless steel put in a sulfur-contaminated process stream encountered in refinery and chemical plants, due to the iron sulfide formation. However, the combination of mixed gases forming iron sulfide has not been fully determined experimentally. In the research, type 304 stainless steel is placed in various mixed gases at elevated temperatures simulated to represent the above processes. The effect of mixed gases on iron sulfide formation is also examined using chemical potential equilibrium diagrams.

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Scientific Key Words: Coatings; Erosion-corrosion; Hot corrosion; Oxidation/ sulfidation; Thermal barrier coatings

Technical Key Words: Fluidized-bed combustor; Furnace wall corrosion; Oil-fired boiler; Gas turbines; Integrated gasification combined cycle (IGCC)

SCOPE OF RESEARCH

Fundamental Approach

The research is on the role of high-temperature oxide scales in the protection of metals, alloys and coatings, with emphasis on their mechanisms of growth, adhesion, protective properties and breakdown in aggressive situations, such as complex and impure environments, very high temperatures, or the simultaneous imposition of external stresses. The research includes fundamental studies of the development of protective scales and has been extended to very corrosive situations where protective scales are not developed nor maintained. Examples include boiler and gas turbine environments, where molten salts may be deposited, and fluidized-bed coal combustion conditions, where impact erosion by solid particles may cause degradation. Extensive programs have also examined the effectiveness of metallic and ceramic coatings for protection against high temperature corrosion.

Applications, Engineering Achievements and Technology Transfer

Most of the laboratory's work is in undertaking fundamental studies of practical situations which underpin development of important hardware and processes in the energy field. These include boilers, fluidized bed combustors, combined-cycle systems, gas turbines and coal gasifiers. The work is often undertaken in conjunction with high temperature corrosion researchers of Nagasaki and Yokohama Research & Development Center in MHI.

RECENT PUBLICATIONS

High Temperature Degradation in Aggressive Gases

1. Nakamori, M., Mizuta, I., Sada, T. and Furuyashiki, Y., "Sulfidation of Water-Wall Tubes in Low-Grades Oil Firing Boilers and Its Prevention by Plasma Spray Coating of Ni-Cr Alloy," Corrosion Engineering, 42, 439-452 (1993).

2. Nakamori, M. and Takahashi, K., "Investigation of Inner Oxidation Rates on Thermal Barrier Coatings," Proceedings for the 41st Corrosion Discussion Meeting, JSCE, P383 (1994).

3. Nakamori, M. and Kanehira, S., "Erosion Corrosion Test Results of SUS310S at High Temperature Corrosion Environment," Proceedings for the 42nd Corrosion Discussion Meeting, JSCE, P491 (1995).

4. Nakamori, M., Kayano, I., Tsukuda, Y., Takahashi, K. and Torigoe, T., "Hot Corrosion and its Prevention in High Temperature Heavy Oil Firing Gas Turbines," 4th International Symposium on High Temperature Corrosion and Protection of Materials, France, May 20-24 (1996).

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Scientific Key Words: Sulfidation; Oxidation/sulfidation/nitridation; Metallizing of ceramics; Diffusion coatings; Nonstoichiometry and mobility in sulfides; Superalloys; Intermetallics; Ceramic/metal joining

Technical Key Words: Fossil fuel-fired boiler, Waste-fired boiler, Fuel cell, Solid oxide fuel cell, Expander turbines, Thermal barrier coating systems; Engineering ceramics

SCOPE OF RESEARCH

Fundamental Approach

This laboratory, Dissimilar Materials Interface Engineering, was re-established in 1994, and current activities are in high-temperature corrosion, non-destructive inspection and ultarsonic microspectroscopy, ceramic/metal joining, development of Zn-Al coatings on steels, and degradation of the thermal barrier coatings. In order to understand the high temperature corrosion processes, it is essential to know the nonstoichiometry and diffusion properties. Examples include non-stoichiometry and mobility of cations in sulfides such as iron-chromium solid solution sulfides and the approach has been utilized to calculate both the sulfide growth rate and cation distributions in the sulfide scale formed on Fe-Cr alloys. Sulfide growth has been observed along the alloy grain boundary, when the Fe-Cr alloys were sulfidized at relatively low sulfur pressures, and sulfide growth mechanisms were investigated, including simultaneous imposition of external stress. Thermal barrier coatings of MCrAlY/ZrO_2 were investigated using several kinds of coating methods such as APS,VPS,HOVF, and the degradation mechanism in aggressive environments containing sulfur and oxygen was established. Engineering ceramics like silicon nitride were joined to metal using active brazing fillers and fracture strengths were evaluated based on fracture tests and FEM analysis. Intermetallic compounds like TiAl are investigated in order to improve their anti-oxidation properties using the novel surface treatment method.

Applications, Engineering Achievements and Technology Transfer

Most of laboratory works are focused on fundamental studies. In some situations, the work is undertaken in conjunction with consortia of industrial partners, as indicated in the following abstracts.

Specific Topics

1. Development of Advanced Materials for Expander Turbine in an Aggressive Environment

This research is being carried out in collaboration with Ebara Research Limited and the aim of the work is to make clear the degradation mechanism of the nickel-based superalloys in sulfur-containing atmospheres at intermediate temperature and further to develop high anti-corrosive materials against sulfidation. Laboratory studies include the sulfidation behaviors of nickel-based superalloys in order to assess and elucidate the grain boundary sulfidation.

2. Non-Destructive Evaluations Using Scanning Acoustic Microscope

In the laboratory an analytical method was developed to determine the stress and strain of the composite materials, and this has been applied to measure the thermal residual stress in the ceramic/metal joint. Based on these techniques, the research is being carried out in collaboration with Hokkaido Medical University and Hitachi Construction Machinery Ltd.. The aim of this work is to estimate the residual stress in artificial teeth made of gold alloys joined to resin, and degradation processes of the alloy/resin joint were assessed.

3. Improvement of Anti-Oxidation Properties of TiAl Alloys at High Temperatures

In the course of sulfidation studies of TiAl alloys, it was found that a $TiAl_3$ layer formed on the TiAl alloy surface due to selective sulfidation of Ti. This $TiAl_3$ phase showed very good anti-oxidation properties, and this sulfidation phenomenon was proposed as a novel surface treatment method to improve anti-oxidation properties of TiAl alloys.

4. Joining Ceramics to Metals

Silicon nitride ceramics are being used for engine parts and turbo-chargers. Laboratory studies are focused on a fracture mechanism of the joints and further on increase in their fracture strength. Si_3N_4/Stainless steel joints with fracture strengths more than 600Mpa are being developed.

RECENT PUBLICATIONS

1. High-Temperature Oxidation

1. Narita, T. and Yoshioka, T., "Sulfidation Properties of Ti-Al Intermetallic Compounds in H_2S-H_2 Atmospheres," Transactions of the Materials Research Society of Japan, 14A, 233-238 (1994).

2. Taumi, H., Narita, T., Nakamori, M. and Harada, Y., "High Temperature Oxidation Behavior of Plasma Sprayed MCrAIY Coatings," Proceedings of the 14th International Thermal Spray Conference, 1, 453-458 (1995).

3. Kawamori, S., Noguchi, M. and Narita, T., "Kinetics and Mechanism of Intergranular Sulfidation of Iron Based Alloys at High Temperatures," Proceedings of the International Conference on Surface Science and Engineering, Beijing, 425-430 (1995).

4. Yoshioka, Y. and Narita, T., "Improvement of Oxidation Resistance of TiAl Intermetallic Compound by Sulfidation Treatment," Zairyo-to-Kankyo, 45, 712-716 (1996).

5. Sato, Y., Hara, M., Shinata, Y. and Narita, T., "Effect of a Small Amount of Hydrogen Chloride on High Temperature Oxidation of Iron-Chromium Alloys," Journal of the Japan Institute of Metals, 60, 841-847 (1996).

6. Noguchi, M. and Narita, T., "Nonstoichiometry in Iron-Chromiu Sulfide $(Fe,Cr)_{1-}S$ at High Temperatures," Journal of the Japan Institute of Metals, 60, 589-594 (1996).

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8. Noguchi, M. and Narita, T., "Sulfidation Behavior of Fe-Cr Alloys in Low Sulfur Pressures," Journal of the Japan Institute of Metals, 60,198-204 (1996).

2. Miscellaneous

9. Narita, T. and Umekawa, H., "Non-Destructive Evaluation of Fracture Strength of Ion-Exchanged Glasses by Acoustic Microspectroscopy," Proceedings of Computer Methods and Experimental Measurements for Surface Treatments, 285-292 (1993).

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11. Matsuura, K., Itoh, Y. and Narita. T., "A Solid-Liquid Diffusion Couple Study of a Peritectic Reaction in Iron-Carbon System," ISIJ International, 33, 583-587 (1993).

12. Matsuura, K., Itoh, Y. and Narita, T., "Effect of Strain on Ferrite Transformation from Super-Cooled Austenite in Fe-0.5%C Alloy," Japan Institute of Iron and Steel, 79, 72-76 (1993).

13. Takashima, T., Yamamoto, T. and Narita, T., "Metallizing of Silicon Carbide Ceramics with Manganese Vapor," Journal of the Ceramic Society of Japan, 101,164-168 (1993).

14. Ohsasa, K., Nakaue, S., Kudo, M. and Narita, T., "Analysis of Solidification Path of Fe-Cr-Ni Ternary Alloy," ISIJ International, 35, 629-636 (1995).

15. Takashima, T. and Narita, T., "Environmental Compatibility of Metal-Ceramic Joints," Zairyo-to-Kankyo, 44, 300-305 (1995).

16. Ishikawa, I., Ogura, Y., Ikeda, S., Suganuma, M. and Narita, T., "Measurement of Sound Velocity Near a Crack by an Acoustic Microscope," Non-Destructive Inspection, 45, 749-755 (1996).

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Scientific Key Words: Breakaway; Oxidation; Oxide-metal interface; Spallation resistance; Steam-side corrosion

Technical Key Words: Advanced steam conditions; Boiler tube failures; Coal-fired boiler; Steam boiler; Ultra-supercritical plant

SCOPE OF RESEARCH

Fundamental Approach

The purpose of the present research is to investigate the oxidation behavior of high-Cr ferritic/martensitic heat-resisting steels in ultra-super-critical (USC) steam. The present research started in April 1997 on a ten-year program (1997 - 2007), as a part of the project “Development of innovative ferritic/martensitic heat resisting steels for USC power plant operating at a steam condition of 650°C and 350 atmospheric pressure”. This project is one of the four big subjects in the “Super Steel Project” in the Frontier Research Center for Structural Materials, National Research Institute for Metals. Basic research is intended in the first stage (1997 - 2002) and applied research in the second stage (2002 - 2007). The impetus for the present research comes from industrial requirements for which steels with good high-temperature oxidation resistance in USC steam, as well as high creep strength, are required. The incentive is that a significant increase in thrust is obtained by increasing the operating temperature. It is now necessary to improve the oxidation resistance of 9 - 12%Cr ferritic/martensitic steels for application to the USC plants at 650 °C, while it is substantially not serious for the plants below 600°C.

In the first stage (1997 - 2002), the research includes fundamental studies on the mechanisms of the development of oxide scale, the scale structure and the spallation of scales. The oxidation tests will be carried out for newly developed steels containing 9 - 12% Cr and other oxidation resistant alloying elements in steam over the temperature range between 550 and 750°C for up to 10000 hours, using small-size sheet specimens. Steam will be generated and heated up to the test temperature in a pre-heater before entering the autoclave. After the tests, the specimens will be weighed to evaluate the kinetics of oxidation. The surface oxide constituents will be identified by X-ray diffraction. The surface and the polished section of the specimens will be examined by a scanning electron microscope and electron probe microanalyzer. The bonding state of ions in the oxides will be also examined by Raman spectroscopy. The oxidation behavior in steam will be compared with that in air and in low oxygen partial pressure environments, such as Ar + O_2 gas, in order to make clear the role of oxygen partial pressure on the oxidation behavior.

Applications, Engineering Achievements and Technology Transfer

The oxidation tests in high-pressure steam and the tests using simulated steel pipes will be performed in conjunction with industrial partners. It is now planned to organize a consortium, or working group, composed of industrial, university and national research institute people in Japan. The oxidation test methods, the evaluation methods and the directions of oxidation-resistant steel development will be discussed. International exchanges are being promoted, such as the exchange of researchers, joint R & D and joint use of facilities, in consideration of the fact that promoting the fusion of various researchers' knowledge through exchanges between R & D institutions and/or researchers is essential for the effective promotion of R & D. The STA (Science and Technology Agency of Japanese Government) Fellowship is one of the systems for invitation of foreign researchers.

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Scientific Key Words: Intermetallics; Oxidation; Heat-resistant steels; Waste incinerator materials; Oxidation/sulfidation; Zirconium/ water/steam

Technical Key Words: Future gas turbine materials; Waste incineration; Heat exchangers; Coal liquefaction; Nuclear power systems

SCOPE OF RESEARCH

Specific Topics

1. High Temperature Oxidation of TiAl

Shida, Y., Dr. and Anada, H., Mr., have studied intensively the modification of oxidation resistance of TiAl by alloying addition. Effects of ternary and quaternary additions of various elements and various new coatings on the oxidation resistance, and on the scale morphologies of TiAl, were the topics of major interest. Also, some studies are underway on the effect of NaCl coating on the surface of TiAl.

2. High Temperature Corrosion in Waste Incineration Systems

Otsuka, N., Dr. and Kundo, T., Dr., have been responsible for a research project on development of corrosion resistant alloys for boiler tube application in Waste-to Energy

Plants. Clarifying the corrosion mechanism in this system is another important topic of this project. Funding is provided by NEDO (the New Energy and Industrial Technology Development Organization of Japan). This project is directed by JRCM (the Japan Research Center for Metals).

3. High Temperature Erosion of Boiler Tube Materials in Simulated PFBC Environments

Otsuka, N., Dr., is the principal investigator of this research. This study has been supported by the Kyushu Electric Power Co. The focus of this research has been on evaluating high temperature mechanical properties (especially high temperature hardness of oxide and sulfide scales formed on boiler tube materials in simulated PFBC environments). These properties are related to the erosion resistance of oxide/sulfide scales at high temperatures.

4. High Temperature Oxidation and Corrosion of Steels in Various Environments

Fujikawa, H., Dr., in collaboration with Tarutani, Y., Mr., Shida, Y., Dr. et al., studied corrosion behaviour of various steels in various high temperature environments. Environments of major interest were automobile exhaust systems, household-stoves, high temperature gas reactor and coal liquefaction.

5. Oxidation Behavior of Zircalloy in High Temperature Steam and Water

Anada, H., Mr., is the principal researcher in this field. Influences of various metallurgical factors on the oxidation behavior of Zircalloy-2 and -4 based alloys have been studied extensively in simulated environments and accelerated laboratory steam environments. Modification of alloys and fabrication heat procedures have also been the item of major interest.

RECENT PUBLICATIONS

1. High-Temperature Oxidation of TiAl

1. Shida, Y. and Anada, H., "Oxidation Behavior of Binary Ti-Al Alloys in High Temperature Air Environment," Materials Transactions JIM, 34, 236 (1993).

2. Anada, H. and Shida, Y., "Oxidation Behavior in Ti-Al Intermetallic Compounds and Their Improvements by Additional Ternary Elements," Sumitomo Search, 52, 83 (1993).

3. Shida, Y. and Anada, H., "The Influence of Ternary Element Addition on the Oxidation Behavior of TiAl Intermetallic Compound in High Temperature Air," Corrosion Science, 35, 945 (1993).

4. Anada, H. and Shida, Y., "Effect of Mo Addition on the Oxidation Behavior of TiAl Intermetallic Compound," Journal of Japan Institute of Metals, 58, 746 (1994).

5. Shida, Y. and Anada, H., "Role of W, Mo, Nb and Si on the Oxidation Behavior of Ti-Al Alloys in High Temperature Air Environment," Journal of Japan Institute of Metals, 58, 754 (1994).

6. Anada, H. and Shida, Y., "Effect of W Addition on the Oxidation Behavior of TiAl Intermetallic Compounds," Journal of Japan Institute of Metals, 58, 1036 (1994).

7. Shida, Y. and Anada, H., "Role of W, Mo, Nb and Si on Oxidation of Ti-Al in Air at High Temperatures," Materials Transactions JIM, 35, 623 (1994).

8. Shida, Y., "How Can the Oxidation Protection of TiAl be Possible?," New Materials (Japan), 6, 63 (1995).

9. Shida, Y. and Anada, H., "The Effect of Various Ternary Additives on the Oxidation Behavior of TiAl in High Temperature Air," Oxidation of Metals, 45, Nos. 1/2, 197 (1996).

2. High Temperature Corrosion in Waste Incineration Systems

10. Otsuka, N., Natori, A., Kudo, T. and Imoto, T., "High Temperature Corrosion of Austenitic Stainless Steels and Ni-Base Alloys in Simulated Waste Incinerator Corroison Environments," CORROSION/93, Paper No. 289 (1993).

11. Otsuka, N., Natori, A., Kudo, T. and Imoto, T., "A 28.5%Cr-40%Ni-1%Mo-0.15%N Alloy Minimizing Fireside Corrosion in Waste Incinerators," CORROSION/94, Paper No. 401 (1994).

12. Otsuka, N., Tsukaue, Y., Nakagawa, K., Yamamoto, A., Kawahara, Y. and Yukawa, K., "An Evaluation of Corrosion Resistant Alloys by Laboratory Corrosion Tests," CORROSION/95, paper No. 565 (1995).

13. Otsuka, N., Ogawa, K., Kudo, T. and Kobayashi, T., "28.5%Cr-40%Ni-1%Mo-0.15%N Austenitic Alloy Minimizing Fireside Corrosion in Waste Incinerators," presented at Stainless Steel '96, June 3-5, Dusseldorf, Verein Deutscher Eisenhuettenleute (1996).

3. High Temperature Erosion of Boiler Tube Materials in Simulated PFBC Environments

14. Hayashida, T., Miyazaki, S., Imaizumi, Y., Ogawa, K., Tokura, S. and Otsuka, N., "Mechanical Properties of Oxide/Sulfide Scales Formed on Boiler Tube Materials in Simulated PFBC Corrosion Environments," CORROSION/95, Paper No. 461 (1995).

15. Hayasida, T., Miyazaki, S., Imaizumi, Y., Ogawa, K., Tokura, S. and Otsuka, N., "High Temperature Erosion of Oxide Scale Formed on T2 and 310HCbN Steels in a Simulated PFBC Corrosion Environment", CORROSION/96, Paper No. 172 (1996).

4. High Temperature Oxidation and Corrosion of Steels in Various Environments

16. Shida, Y., Fujikawa, H. and Sawaragi, Y., "The Oxidation and Carbon Transfer Behavior of Ni-27Cr-5Mo-5W Alloys in an Impure Helium Atmosphere," Corrosion Science, 34, 1157 (1993).

17. Kitayama, S., Shida, Y., Ueda, M. and Kudo, T., "Development of Corrosion Resistant Titanium Alloys for Severe Oil Wells," Sumitomo Search, 52, 67 (1993).

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20. Fujikawa, H. and Shida, Y., "High Temperature Oxidation of Si-Bearing Ferritic Stainless Steels in Humidified Atmosphere," Zairyo-to-Kankyo (Japan), 45, 350 (1996).

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5. Oxidation Behavior of Zircaloy in High Temperature Steam and Water

25. Anada, H., Shida, Y. and Kodama, T., "Nodular Corrosion Behavior in Zircalloy-2 and Zircalloy-4 Under Various Solution Treatment Conditions," Sumitomo Search, 52, 118 (1993).

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27. Anada, H. and Kiyoko, T., "Microstructure of Oxides on Zircalloy-4, 1.0%Nb-Zircalloy-4 and Zircalloy-2 Formed in 10.3MPa Steam at 673K," Zirconium in the Nuclear Industries, ASTM-STP 1295, Eds. E.R. Bradley and G.P. Sabol, 12 (1996).

28. Anada, H., Herb, B.J., Nomoto, K., Hagi, S., Graham, R.A. and Kuroda, T., "Effect of Annealing Temperature on Corrosion Behavior and ZrO_2 Microstructure of Zircalloy-4 Cladding Tube," Zirconium in the Nuclear Industries, ASTM-STP 1295, Eds. E.R. Bradley and G.P. Sabol, 33 (1996).

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Scientific Key Words:	Ceramic oxidation; Ceramics degradation/interfaces/ coating; Gas-solid reaction kinetics; Pesting; Refractory metals; Silicides
Technical Key Words:	Engine materials; Aeroengines; Ceramic turbine blades; Future gas turbine materials; Surface engineering

SCOPE OF RESEARCH

This laboratory was newly founded in 1994. The research activity is directed towards understanding of structure and properties of anodic oxide films, oxide scales formed at high temperatures, and interfacial reaction layers between solids. Current investigational works on high-temperature materials are focused on a fundamental approach.

Specific Topics

1. Oxidation Behavior of Ultra-High Temperature Materials

Oxidation of SiO_2-forming materials such as Si_3N_4,SiCand $MoSi_2$ at ultra-high temperatures is being carried out. The aim is to clarify the oxidation behavior of ultra-high temperature materials. Especially, emphasis is placed on the effect of a second phase such as additives and reinforcement materials on the oxidation resistance of ultra-high temperature materials.

2. Solid-State Reactions Between Metals and Ceramics

The interfacial reactions in metal/ceramic(SiC or Si_3N_4) systems at high temperatures are being investigated. The reactions are grouped into three modes, (A) silicide formation, (B) silicide+carbide (or nitride) formation, and (C) Si+carbide (or nitride) formation. The aims are to clarify the interfacial reaction behavior between metal and ceramic, and to estimate the maximum application temperature of metal-ceramic composites.

3. Research and Development of Ultra-High Temperature Materials

Composites such as carbon/silicide, carbon/Si-based ceramic, refractory metal/silicide, refractory metal/Si-based ceramic, and silicide/Si-based ceramic are expected to be effective as ultra-high temperature materials having high oxidation resistance. Preparation of these composites is being carried out by a spark plasma sintering method, and the evaluation of the oxidation behavior and mechanical properties of the composites is also being carried out.

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Scientific Key Words: Alumina; Cyclic oxidation; Impurities; Intermetallics; Ion implantation; Preoxidation; Surface treatments

SCOPE OF RESEARCH

1. Oxidation of Intermetallic Compounds

Considerable effort has been spent in our laboratory on studies of the oxidation behavior of TiAl, which is a base material having high specific strength at elevated temperatures. Turbine blades, engine valves and turbocharger rotors made of TiAl-base alloys are under various tests for practical application. However, a certain set of knowledge is still lacking for the comprehensive understanding of the influence of alloying additions and gaseous species on their oxidation behavior. The objective is to provide new knowledge regarding the above two factors. Various surface treatments were also performed to examine their potential in providing protection against oxidation. As a result it has been found that small alloying additions of Hf or Zr are very effective to improve the oxidation resistance both under isothermal and thermal cyclic conditions in an oxygen atmosphere. This is attributable to the formation of protective Al_2O_3 scales in a temperature range 1100 to 1300 K. Further increases in the temperature and in the additive content decrease the effect.

An ion implantation technique was used to locate Al, Si, Ar, Cr or Nb in the surface layer of TiAl. Implantation of Si, Cr or Nb at a dose of 10^{21} ions m^{-2} was found also to be very effective in forming protective Al_2O_3 scales which can survive under thermal cycling conditions with the temperature varying between room temperature and 1200 K for at least 1000 ks. The influence of gaseous species is being studied. Carbon dioxide and water vapor enhance the oxidation very much, while nitrogen enhances it to a smaller degree. The partial pressure of oxygen also influences the oxidation behavior. Preoxidation under low partial pressure of oxygen was found to be effective to form protective Al_2O_3 scales.

The oxidation behavior of Ti_3Al and Ti_3Al-Nb was studied and the influence of Nb and nitrogen gas in the atmosphere was considered.

The oxidation behavior of Ti_5Si_3, which is a candidate as a structural or coating material in the temperature range 1300 to 1500 K, was studied. This range is too high for TiAl-base materials and too low for $MoSi_2$. Ti_5Si_3 forms a protective scale consisting mainly of SiO_2 in the temperature range 1400 to 1500 K. Breakaway takes place at 1550 K in air. This is explained in terms of the appearance of TiO_2 particles in the SiO_2 scale.

2. *Fe-Cr-Al Alloy Foils*

In order to improve the life of a metal honeycomb, used as the catalyst support for an automobile exhaust gas system, Al-deposited Fe-20Cr-5Al foils containing rare earth elements were manufactured and their oxidation characteristics were examined. These foils gave the smallest parabolic rate constants ever reported among alloys of similar compositions, with the activation energy of oxidation comparable to reported values. The total Al content was around 5 mass %. However, the oxidation took place on the surface where the Al concentration was rather high, though most of the Al deposited diffused into the substrate during heating to a test temperature. The detailed metallographic examinations revealed that the Al_2O_3 formed on the foil shows definite transformation stages such as γ- to θ- to α-Al_2O_3, whereas α-Al_2O_3 appears much earlier with the conventional foil. A TEM study showed that these transformations take place at the scale/substrate interface.

3. *Low-Carbon Steels*

The recycling of steel scrap is receiving considerable attention in developed countries. Although the recycling is necessary and has a large merit in relation to energy saving and prevention of air pollution, a few harmful impurities are enriched as the number of recycles increases. The descaling characteristics are being studied for low-carbon steels containing relatively high concentrations of Cu, Sn, or Si which would be included in the scrap. The mode of scale failure, thermal stress and mechanical stress in the scale will be assessed.

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Scientific Key Words: Superalloys; Structural ceramics; Thermal barrier coatings; Waste incinerator materials; Creep/corrosion interactions; Creep/fatigue-oxidation interactions; Corrosive failure analysis

Technical Key Words: Engine materials; Thermal barrier coating systems; Future gas turbine materials; Ceramic turbine blades; Municipal waste-burning

SCOPE OF RESEARCH

Fundamental Approach

The strategy of the whole research activities is based on the policy that how to simulate reasonably the actual service condition of different kinds of high temperature structural components, such as gas turbine blades and boiler tubes in laboratory experiments, particularly from many aspects of thermal (temperature)-chemical (corrosivity)-mechanical (stress) loadings. Therefore, the thrust of this research is always based on the failure analysis of the high temperature components subjected to damage in practical service. Then, the aggressive environmental effect, such as hot corrosion, on mechanical failure such as creep, fatigue and creep/fatigue interaction is emphasized along with inversely the stress effect on the high-temperature corrosion. Current research activities are mainly focused on the mechanical failure of advanced coating systems, including some thermal barrier coatings in aggressive environments. Furthermore, materials R&D for the more complicated corrosive environment, such as in high-temperature municipal waste incineration plants, also is conducted in a link of the national project research.

Applications, Engineering Achievements and Technology Transfer

Most of the experimental research is conducted to get fundamental knowledge and/or information which can contribute to the R&D of high-temperature material systems in the energy field, in particular for electric power generation. This includes gas turbines, boilers, different kinds of chemical reactors, and waste power generators. The work is frequently undertaken in conjunction with consortia of industrial partners, as indicated in the following abstracts.

Specific Topics

1. Hot Corrosion Mechanism of Advanced Superalloys with Controlled Crystallinity

Hot corrosion resistance, as one of the life limiting factors for the high temperature structural components, was investigated in connection with the corrosive failure analysis for some kinds of advanced superalloys, including the controlled crystalline alloys, on the basis of comprehensive analyses of the thermodynamic and kinetic approach, with support of the analytical data of microstructure. The role of the compositional and microstructural factors on hot corrosion behavior was quantitatively evaluated through extractive evaluation and regression analysis from the complicated factors, and furthermore a reasonable hot corrosion model was proposed.

2. Failure Analysis of Thermal Barrier Coating Systems under Different Combinations of Thermochemical (Corrosive) and Thermomechanical (Stress) Loadings

Two kinds of thermal barrier coating (TBC) systems were characterized and subjected to different aspects of the property evaluations, such as high-temperature oxidation and hot corrosion resistance, and the corrosion-creep failure resistance which is a very important factor from the practical viewpoint. In particular, on the basis of the failure analysis for the specimens obtained from such a various testing methodology, a basic guideline for the optimized TBC systems was discussed and proposed.

3. R&D for the Advanced Material Systems of Highly Corrosion-Resistant for High Efficiency Municipal Waste Power Generation

R&D of advanced material systems for the heat-exchanger, with corrosion-resistance much higher than for the existing materials, is one of the key technologies to establish high-efficiency municipal waste power generation. In the present study, the systematic investigation has been conducted about both the analysis of the corrosive environment in the much higher temperature waste incineration plant and the R&D of high performance material systems, along with the optimized material evaluation methodology. In particular, the applicability of some kinds of the thermal spray coating systems, with different corrosion-resistant alloys as the coating materials, was evaluated by means of the reasonably simulated laboratory corrosion test with and without cyclic heating.

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Scientific Key Words: Aluminides; Cyclic oxidation; Intermetallics; Oxidation; Preoxidation; Titanium alloys/aluminides

Technical Key Words: Airframe materials; Engine materials; Compressors; Future gas turbine materials; Rotors

SCOPE OF RESEARCH

Scientific Aspects

The research is aimed at clarifying the high-temperature oxidation behavior of intermetallic alloys. The research includes studies about oxidation rate, scale growth, scale adhesion and oxides formed during oxidation, mainly in cyclic oxidation. The effects of additional elements, influence of microstructure and atmosphere are also investigated to find out the way to improve the oxidation resistance of the alloys.

Applications, Engineering Achievement and Technology Transfer

The research is focused on intermetallic compound TiAl and TiAl-based alloys (gamma alloys). These alloys are expected to be new right-weight, heat-resisting materials. However, their oxidation resistance is much inferior to the conventional heat-resisting materials, such as Ni-based superalloys. This is one of the reasons impeding these materials from practical use. The oxidation behavior is affected by oxidation temperature, alloy composition and additional elements. Influence of the microstructure is relatively small. Concerning the alloy composition, appropriate addition of Nb and W is effective to improve the oxidation resistance. The improvement is also achieved by the heat treatment in a low air pressure atmosphere in the vicinity of 10^{-3}Pa, because of thin alumina scale formation. In collaboration work with Kim, Y-W., Dr., time-to-rupture in a creep test was found to be prolonged by this heat treatment without damaging the fatigue property of the alloy. The mechanism of outer alumina scale formation during the treatment is under investigation.

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INDEX OF SCIENTIFIC KEYWORDS

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