High Temperature Corrosion Research in Progress: 1997

(K through U)

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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

EPRI would like to recognize the following individuals whose contributions have made this report possible:

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

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Scientific Key Words:	Alumina; Chromia; Oxidation/sulfidation; Intermetallics; Thermal barrier coatings
Technical Key Words:	Gas turbine combustors; Superalloys; Thermal barrier coating systems

SCOPE OF RESEARCH

Fundamental Approach

The aim of the research is to investigate the role of high temperature oxide scales for the protection of metals, alloys and coatings. Research areas are fundamental studies of oxide scale growth mechanisms, protectiveness and breakdown in hostile environment at high temperature.

Applications, Engineering Achievements and Technology Transfer

Most of the work in the laboratory is carried out to elucidate fundamental aspects of practical situations and to provide important data, which are related in high temperature oxidation.

Specific Topics

1. *High Temperature Oxidation of Thermal Barrier Coatings on Combustors in Gas Turbines*

This work is being carried out under sponsorship of Korea Electric Power Corporation to develop parts of the combustors in gas turbine.

2. High Temperature Oxidation of Stainless Steels

This work is to minimize surface defects of stainless steel, which are likely to form in the steel mill, under sponsorship of Pohang Steel Corporation in Korea.

3. High Temperature Oxidation of Rapidly Solidified Materials

This work is to develop advanced materials for metallic catalyst honeycomb.

RECENT PUBLICATIONS

1. High Temperature Oxidation

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2. Son, I.R. and Kim, G.M., "A Study on the Formation of Oxide Scale on the Stainless Steels at High Temperature," Journal of the Korean Institute of Surface Engineering, 27, 123-133 (1994).

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2. Miscellaneous

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Scientific Key Words: Flue gas; Erosion-corrosion: steels, coatings, refractories; Chlorine; Deposits; Inorganic coatings; Life prediction; Modeling erosion-corrosion; Borides; Coating durability/adhesion; Diffusion coatings; Erosion corrosion of coatings; Pack cementation coatings; Bond/thermal barrier coatings; Hot corrosion; Zirconia ceramics; Wear; Abrasion resistance

Technical Key Words: Coal-fired boiler; Combined cycle system; Fossil fuel fired boiler; Fuel quality effects; Steam turbine; Gas turbines; Thermal barrier coating systems

SCOPE OF RESEARCH

Specific Topics

1. Materials for Flue Gas Desulfurization Systems

This research will study the corrosion behavior of the materials for flue gas desulfurization systems under construction in Korea, aiming at the improvement of the life of the systems. By treating flue gas containing SO_2 using wet limestone slurry, the systems suffer from corrosive and erosive environments, which lead to failures of construction materials due to pitting, crevice corrosion, or stress corrosion cracking on metals, or erosion-corrosion on polymeric and ceramic lining materials. The research includes studies on the corrosion and erosion mechanism in an open reaction system under the conditions of varying temperature, moisture and acidity, sometimes under stress. Simulated reactors will be set up for the investigation, and the test results will be analyzed in view of the conventional corrosion theory and theory of chaos. The theory of chaos will give a new perspective in understanding the fundamental mechanism of degradation of materials under diverse conditions occurring in the system. Computer simulation for a model system will be conducted to give the reliability of the interpretation of measured data and vice versa. The research will also give emphasis on the characterization of corrosion-erosion properties of amorphous coatings obtained by means of a high velocity spray. Amorphous coatings are recently considered to be very promising protective layers for FGD systems.

The results of the investigation will be submitted for the preparation of repair guidance for the operating systems. The results will also be used as a guideline for FGD systems constructed in the future, especially in selecting materials economically. The development of a computer simulation program will serve as a tool for the life prediction of the system and give proper information about repairing and substitution of failed parts. Based on the results, the applicability of amorphous coatings to the FGD systems, is also reported.

2. Boron Diffusion Coatings to Protect Turbine Nozzle Boxes

This research studies boron diffusion coatings used to protect turbine nozzle boxes from erosion due to solid particles. The emphasis of the research is on kinetics and mechanisms of growth, as well as assessment of erosion resistance of the applied coatings. Key technologies of the research include a study of microstructures at the interface between the coating/substrate with alloy addition in order to optimize the protection properties of the coating layer under steam turbine environments, where solid particles cause erosion of the materials, and development of the simulation program which can estimate the life of the coating layer under steam turbine field condition. Additional studies will be carried out on the degradation mechanism of the coating layer under cyclic oxidation environment at high temperature and the effectiveness of metallic alloys for protection from the high-temperature erosion-corrosion environment.

This research is being carried out as a new project from 1997 in collaboration with a few universities under the sponsorship of the Korea Electric Power Research Institute. The work is also connected with industrial partners. The overall objectives of the research are to extend the life of the turbine nozzle box and partial boride coating on the nozzle blade and to develop a simulation program which is able to evaluate the coating layer for use in steam turbine. Laboratory erosion-corrosion studies on the boride coating layer will be carried out with the tester which is able to control erosion variables, such as particle size distribution, density, velocity, and alloy composition at steam turbine conditions. In addition to these variables, the composition of the material and other environmental parameters, which influence the properties of the coating layer will be evaluated in order to clarify mechanisms of degradation or protection of the materials. The study will also cover the effectiveness of multi-metallic coatings for protection from erosion-corrosion under multiple impact conditions. Based on degradation and protection mechanism, the optimum protection coating will be applied in the turbine nozzle box under field conditions.

3. Influence of Thermal Barrier Coatings on Efficiency and Reliability of Gas Turbines

The purpose of this research is to increase the efficiency and reliability of the gas turbine by applying thermal barrier coatings on turbine blades. The coatings provide protection for the base metals of the turbine blades from hot and dusty gas. The key technology of the research includes zirconia coatings produced by electron beam plasma enhanced deposition (EBPVD) and MCrAlY (M=Ni or Cr) bond coatings obtained by high velocity oxygen fuel spray. The research comprises studies on the mechanism of the deposition of zirconia coatings, on the efficiency of the thermal barrier coatings in terms of microstructure and on the relation between the deposition rate and thermal stress. The research also comprises studies on the diffusion behaviour of aluminum in the MCrAlY bond coatings, in terms of alloying elements, and on the relation between durability and oxides at the interface.

This research is being carried out in collaboration with KIST (Korea Institute of Science and Technology) under the sponsorship of the Korea Electric Power Research Institute. The work will be extended to the construction of the coating facilities for the application of thermal barrier coatings to real turbine blades and to the testing of the reliability of the system.

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Scientific Key Words: Surface treatments; Interdiffusion; Intermetallics; Electrochemical methods; Metal; Coatings; Vacuum-sputtered coating

Technical Key Words: Microelectronics

SCOPE OF RESEARCH

Much of the research uses X-ray diffraction methods to study interdiffusion of electrodeposited and sputtered layers but certain aspects are not relevant to high-temperature corrosion.

Specific Topics

1. The layer structure and phase stability at thermal treatment (at 200, 300, 350 and 450°C up to 200 hours) of electrodeposited 0.3 - 2 microns thick Au, Fe-80Ni, Ni-B alloys have been investigated by transmission and scanning electron microscopy and X-ray diffraction analysis.

2. In a layer system Au/Fe-Ni80/Cu during the process of electrodeposition, Fe-80Ni develops into Ni_3Fe without free Ni or Fe. During thermal treatment at 350°C for 100 hours an intermetallic AuCu layer forms in this system, changing the Au structure.

3. In a layer system Au/Ni-B/Cu, the electrodeposited amorphous Ni-B layer contains 6.45 - 6.8 wt% of B and $(3.2 - 6)\cdot 10^{-2}$ wt% of C. Although the Ni-B layer transforms as crystallization occurs at 300°C (200 hours) and results in formation of borides (Ni_3B, Ni_2B), the structure and phase stability of a 0.3 - 1 micron thick Au layer remains stable until thermal treatment up to 350°C for 200 hours.

4. The complete destruction of the electrodeposited golden layer structure in the layer system Au/$Ti_{sputt.}$/ceramics occurs at thermal compression for 350°C for 200 h. The chemical composition of the sputtered layer in this case is as follows (wt%): Al - 0.45-0.88; Cr - 0.019; Fe - 0.0428; Ni- 0.019; Zr, V - 0.016-0.0073; Sb, W, Ta - (1.06-4.5)$\cdot 10^{-5}$; As - (6.0-7.0)$\cdot 10^{-4}$. The destruction of the Au structure and worsening of its adhesion and the growth of Au monocrystals is determined by formation of intermetallics Au_2Ti, $AuTi_3$ at 350°C (150 h) and 450°C (50 h).

These investigations on the changes of structure and phase composition of thin metal layers are of essential importance for selection of such layer systems for utilization in electronics and microelectronics, as well as in apparatus construction. The results of the layer structure and chemical composition investigations of Sn, Fe-80Ni and Ni-B electrodeposited from different electrolytes layer structure allow forecast of the choice of optimal electrodeposition technology to ensure the interadhesion of metallic layers, their structure and phase stability and necessary electro-physical properties in the aggregate.

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MEXICO

CONTENTS

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Scientific Key Words:	Heat-resistant steels; Hot corrosion; Creep/corrosion interactions; Temperature sensors; Life prediction; Thermal barrier coatings; Electrochemical measurements and monitoring
Technical Key Words:	Oil-fired boiler; Condensate (dew-point/downtime) corrosion; Pressure vessel alloys; Heat exchangers; Thermal barrier coating systems; In-plant monitoring

SCOPE OF RESEARCH

Fundamental Approach

The useful life of superheaters and reheaters of power stations that use heavy oil as a fuel are shortened and their continuous service is inhibited by corrosion and creep type problems. The increase of corrosion attack of boilers is caused by the presence of fuel ash deposits containing mainly V, Na and S that form low melting point compounds. In this context, the tubes are exposed to the action of high stresses and high temperatures producing so-called 'creep damage'. In this research, two kinds of studies are reported: laboratory and field studies using a ferritic and austenitic type steels. The laboratory research includes fundamental studies of the development of protective scales, gravimetric and electrochemical measurements and thermal barrier coating systems resistant to hot corrosion. The field research includes fire-side metal temperature and ultrasonic measurements, in order to find relationships between corrosion rates and metal temperature for the different heat exchanger steels used in heavy oil-fired boilers. Furthermore, some electrochemical monitoring was performed in low and high temperature equipment. Some elements of a power station were coated with different types of coatings containing Cr and Si, using the powder flame spraying technique.

Applications, Engineering Achievements and Technology Transfer.

From the materials standpoint, the degradation of high-temperature boiler components exposed to V-, Na- and S-rich environments remains unsolved. So, most of the laboratory's work is in undertaking fundamental studies of practical situations which underpin development of important software, hardware and processes in the energy field. These include the oil-fired boilers, petrochemical industry and industry furnaces. The work is often undertaken in conjunction with consortia of industrial partners, or single sponsors.

Specific Topics

1. High Temperature Corrosion of 150MW Babcock-Hitachi Steam Generator Design

This research is being carried out in collaboration with Comision Federal de Electricidad (Electricity Generating Board) and Consejo Nacional de Ciencia y Tecnologia (CONACyT). The overall aim of the work is to develop:

- Electrochemical techniques for high temperature applications (monitoring).
- Development of high temperature corrosion resistance coatings (Cr and Si).
- Relationships between corrosion and metal temperature in a steam generator that uses heavy-fuel oil as a fuel.
- Relationships between metal temperature, steam temperature, gas temperature and wall thickness measurements.
- Life prediction software for high temperature reheater and superheater materials.

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Scientific Key Words:	Thermodynamic modeling; Computer modeling; Interdiffusion; Interface microstructure and microchemistry; Ceramics oxidation; Ceramics corrosion; Refractory materials; SiAlONs; Silicon nitride; Silicon carbide
Technical Key Words:	Waste incineration; Furnace wall corrosion; Municipal waste-burning; Membranes; Ceramic heat exchangers; Ceramic turbine blades; Glass melt furnaces; Superstructure refractories; Alkali vapor attack; Oxy-fuel firing; Laboratory simulation of refractory corrosion

SCOPE OF THE RESEARCH

Fundamental Approach

The thrust of the research is on the study of the formation of oxide layers on ceramics, with emphasis on their mechanism of growth (thermodynamics and kinetic) and adhesion (mechanical stresses, thermal cycling). The research includes the computer modeling of the layer formation on the ceramics. Using thermodynamic and kinetic data, the nature and the progress of layer formation is predicted. Thermodynamic modeling of the interaction of refractories with glass melt vapors (especially alkalis) is performed. Laboratory studies on the interaction mechanisms of superstructure refractories and glass melt vapors are carried out.

Practical Applications, Engineering Achievements and Technology Transfer

Up till now, the work of the laboratory is undertaken in fundamental studies of corrosion behaviour of ceramic materials in gas atmospheres and metal melts. Together with the Solid State Chemistry Group of Metselaar, R., Prof. and van Loo, F., Prof. (Eindhoven University of Technology) model calculations of layer formation and diffusion paths were performed in model systems. Recently, work was started in modeling corrosion processes in real systems. The influence of fluorine, chlorine and sodium present in the material or atmosphere is taken into account. Conditions prevailing in glass melt furnaces, waste incineration and aluminum melting are translated to computation parameters in the models

Reduction of the refractory corrosion is performed by process measures and optimal choices of refractory materials in view of:

- extended furnace lifetimes
- reduction of refractory related glass defects
- improvement of thermal insulation of glass furnaces.

Specific Topics

1. Corrosion Behavior of Refractories in the Combustion Chamber of Oxy-Fuel Fired Glass Furnaces

The main analysis techniques used are XRF, XRD and ICP. TNO has conducted both industrial (field) tests and accelerated laboratory vapour phase corrosion tests. For industrial tests, several refractory samples (silica, fused cast AZS, fused mullite, zircon) were placed in the flue gas channels of oxy-gas fired furnaces at temperatures between 1300 and 1400°C. In addition, the chemical and crystallographic profiles of used silica bricks from the crown of both air-gas and oxy-gas fired soda-lime glass furnaces were analysed accurately at the hot face of silica bricks from the oxy-fuel furnace, increased Na_2O surface concentrations, up to 2.5 wt%, were measured, compared with 0.5-1 wt% for silica bricks from the air-fuel furnace. Furthermore, it was observed that the glassy phases occurring from the reaction between the silica surface zones and the NaOH vapors have a typical soda-lime composition (68-70 wt% SiO_2, 11-12 wt% Na_2O and 10-14 wt% CaO for the oxy-fuel case). Preliminary thermodynamic calculation indicated that, under oxy-fuel conditions, stable sodium-rich silicate glass phases can be formed up to higher temperatures than under air-fuel conditions. This implies that under oxy-fuel conditions, low viscosity Na-rich silicate glass phases are formed at the higher temperature, near surface zones of the silica bricks, resulting in accelerated dripping and corrosion. Currently, the thermodynamic calculations and laboratory experiments are being extended to account for the effect of CaO in the silica on the corrosion behavior and to the study the vapour phase attack of alternative refractory materials.

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Scientific Key Words: Erosion-corrosion; Creep; Sulfidation; Spallation; Lifetime

Technical Key Words: Low-NO_x firing; Coal gasification; Corrosion monitoring; Supercritical coal-fired boilers; Gas turbines

SCOPE OF RESEARCH

Fundamental Research

The main interest is the spalling of oxide, erosion corrosion and the interaction of corrosion, creep and thermal fatigue. Test environments are superheated steam, water steam mixtures and sulfidizing and chloride-containing gases, as in coal gasification, Low NO_x firing and waste incineration.

Applications, Engineering Achievements and Technology Transfer

Most of the work has been sponsored by the Dutch electricity companies. Only in some projects cosponsoring is applied; cooperation in European COST projects is more common. The relevant projects are summarised in the following abstracts.

Specific Topics

1. Sulfidation Resistance Under Creep and Cyclic Strain-Compression Conditions

Thermomechanical interactions of low-alloyed and high-alloyed materials, with corrosive gases, is examined by means of slow strain rate and fatigue experiments. Microscopic examinations of the corrosion scales are done by means of advanced optical methods and scanning electron microscopy. By means of optical interference contrast microscopy, in combination with SEM/EDS analysis, the structure and morphology of the corrosion scales are examined. Materials are ranked on their resistance to cracking under corrosive conditions. Because shut-down corrosion plays an important role in coal gasification, this aspect is also studied extensively by means of electrochemical tests.

2. Reconditioning of Gas Turbine Materials

Superalloys in gas turbines and thermal barrier coatings on turbine blades have to be reconditioned during the lifetime of the turbine. By means of extensive microscopic characterisation of the materials after various heat treatments, knowledge for the best rejuvenation procedures is obtained.

3. Spalling of Oxide in Superheated Steam

In a superheated steam loop, tubes are exposed in combination with external stresses to simulate the conditions of ultrasupercritical boilers. The oxide layers on the test tubes and on tensile specimens are examined on spallation. The fracture strains of the oxide layers on the tensile specimens are determined under tensile as well as under compressive straining.

4. Erosion Corrosion of Carbon Steel in Wet Steam

Already in the period 1960 up to 1980, much research has been done on erosion corrosion in wet steam systems. KEMA found that small amounts of the elements Cr, Cu and Mo in carbon steel have a very pronouncing effect on erosion-corrosion resistance. Aside from the best water treatment and flow conditions, the choice of an erosion-corrosion-resistant modified carbon steel should be made in erosion-corrosion sensitive components of conventional and nuclear power production units. It prevents not only many leakages in the system but it decreases also the amount of dissolved iron in the system. To come to a breakthrough in the application of modified C-steel, computer models are made for calculating the dependence of erosion-corrosion on chemical water treatment, physical flow conditions and carbon steel quality, as well as Return On Investment calculations for the modified carbon steel.

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Technical Key Words:	Coal gasification; Fluidized bed combustor; Combined cycle system; Gas turbines; Ceramic heat exchangers; Catalyst support systems; Ethylene pyrolysis

SCOPE OF RESEARCH

Fundamental Approach

A multi-disciplinary group of scientists and technicians is responsible for executing the European Commissions' own Framework R and D programme concerned with materials behaviour at elevated temperatures in industrially-relevant corrosive atmospheres, i.e. complex multi-component gas mixtures, solid ash deposits, molten salts and aqueous condensates. An in-depth understanding of the mechanisms responsible for the degradation of alloys, coatings, ceramics and composites is being established under conditions where oxidation, sulfidation and/or carburization can occur; the influence of Cl-containing species is also studied. Reaction kinetics are established by both mass-change and cross-sectional penetration measurements. The interactive effects of creep and corrosion are also being studied for a range of oxidizing and reducing environments. Temperatures cover the range 400 to 1700°C involving exposures from a few minutes to thousands of hours. The major thrust of these studies is directed at understanding the degradation processes involved and thus to assist in optimising material composition as well as techniques by which surface scales can be formed, or coatings applied, which confer protection. Scale nucleation and growth as well as scale spallation studies are an integral part of these investigations. Studies are also concerned with the performance and ageing of ceramic catalytic support structures under conditions simulating those encountered in automobile exhaust systems.

Applications, Engineering Achievements and Technology Transfer

Studies are carried out in gaseous, solid or liquid environments of relevance to process atmospheres found in a broad range of industries, including the petrochemical, power generation (coal gasification and fluidized bed combustion), and transport (land, sea and air) industries, as well as others associated with specific manufacturing processes. Observations on probes exposed in pilot and commercial plant enable the relevance of such laboratory tests to be established. This has been aided by inserting a range of pure metals and compounds in plants, thereby allowing the character of the hot process atmospheres to be defined better, prior to a comparison with the laboratory-derived data. In addition to carrying out generic-type studies of general use to industry, more specific investigations are targeted to the specific needs of third parties, in the form of collaborative or multi-client studies, or on a confidential basis as research contracts for industrial sponsors or research organisations.

Specific Topics

1. Gaseous Atmospheres

Gaseous corrosion studies are carried out in complex, multi-component mixtures which are either in thermodynamic equilibrium, or which flow through the reaction vessel at a rate sufficiently high to prevent equilibration occurring (a situation more relevant to that occurring in most industrial plants). The test rigs have been specially developed for use with potentially toxic and explosive species at temperatures up to 1500°C. A rig is also being used with Cl-containing gases. Important environmental parameters which influence gaseous corrosion in mixed oxidizing/sulfidizing/carburizing atmospheres are being assessed and the mechanisms of degradation and protection elucidated. Studies are assisted by in-situ nucleation and growth studies using a hot-stage microscope fitted with an environmental chamber and top-mounted video camera. A thermocycling rig for complex environments at temperatures up to 1500°C is also available. Continuous kinetic studies are carried out in thermobalances, modified to accommodate toxic/corrosive gases.

2. Solid Ash Deposits

The influence of the presence of solid fly-ash upon corrosion behaviour is studied using mixtures of real and synthetic ashes coated onto material surfaces with periodic renewal of the deposit necessary. The presence of uncombusted carbon and chloride-containing salts is being evaluated over a range of temperatures as well as studying the synergistic influence of incorporating down-time cycles in dry or moist air at room temperature.

3. Molten Salts

Hot corrosion studies in the presence of molten salts are carried out in low velocity burner rigs in which aviation or marine fuels are burnt in air. Controlled amounts of contaminants can be introduced via atomisers positioned up-stream of the combustion chamber. The influence of variations in fuel composition, particularly sulfur, as well as the presence of various Na-containing contaminants is being quantified for metallic, ceramics and composite materials. In addition, two of the burner rigs offer the possibility to cycle specimens thermally by retracting them from the hot gases at temperatures up to a maximum of 1400°C.

4. Creep-Corrosion Interaction

The interactive effects of deformation and corrosion are studied in a range of oxidizing and reducing atmospheres at temperatures up to 1000°C. Different multicomponent gas mixtures are applied. Additionally the influence of salt deposits and ash coverage is investigated. Single specimen creep rigs have been specially equipped with environmental chambers making them suitable for investigations involving the use of aggressive environments. The ability of surface oxides to remain adherent and thereby confer long-term protection to the substrate under constant strain-rate conditions is being evaluated. Factors governing the healing of cracks formed in the surface scale are an implicit part of these studies.

5. Corrosion Data Management

All of the raw corrosion data generated can be handled on a daily basis by a Corrosion Test Management system (CTM) specially developed to encompass the wide variety of types of tests being carried out. Conventional experimental data and microstructural images are both handled by this system. After validation, test results are transferred to a High Temperature Materials Corrosion Data Bank (HTM-CDB) which is accessible by external clients.

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Scientific Key Words:	Life prediction; Corrosion; Hydrogen attack; Creep/corrosion interactions; Pressure vessel alloys; Weldments; Coatings
Technical Key Words:	Fluidized-bed combustor; Waste incineration; Evaporators; Superheaters; Membrane Waterwalls; Hydrogen vessels; Hydroprocessing units

SCOPE OF RESEARCH

Most of the work is undertaken in conjunction with consortia of industrial partners. Studies on erosion-corrosion of evaporator tubes in a fluidized-bed combustion pilot plant have been completed. Subsequent projects are directed to waste-to-energy installations. The applicability of highly alloyed materials for waste-incinerator superheaters is determined. The present steam conditiond are 400°C/40 bar. The objectives are to improve the component lifetime and the availability of the plant. For future systems the use of higher metal and steam temperatures to obtain higher efficiencies is investigated. Both laboratory and plant exposures are carried out. Both high alloyed materials (Alloy 28, Alloy 45TM, Alloy 625) and coatings were tested. In addition research is initiated on protection systems for waterwalls. Part of the national programmes are carried out within the European collaboration COST 501.

In order to increase the conversion yield and the efficiency of hydrotreating processes, key components are subject to improvements. The behaviour of welded components made from new steel grades is assessed to predict the integrity of pressure vessels in hydrogen under creep conditions in the temperature range from 350°C to 600°C. Hydrogen-creep interactions are studied, and welded components are operated under realistic hydrogen service conditions. Part of the investigations are carried out within the European Brite-Euram programme.

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Scientific Key Words: Alumina growth; Ceramic coatings; Chemical vapor deposition; Chloridation; Chromia; Cyclic oxidation; Deposits; Electrochemical measurements; Intermetallics; Molten glasses; Molten salts; Oxidation/sulfidation; Platinum-modified aluminides; Salt deposits; Salt melts

Technical Key Words: Engine materials; Fuel cells; Molten carbonate fuel cells; Future gas turbine materials; Heat exchangers

SCOPE OF RESEARCH

Fundamental Approach

The main research goal is to increase the number of applications of various coated and uncoated alloys in aggressive environments at temperatures ranging from 400°C to 1100°C. To this end, the fundamentals of degradation mechanisms are studied in gaseous, molten salt and under deposit environments. The information obtained from these studies includes transport mechanisms through oxide layers, adhesion/de-adhesion mechanisms of oxide scales and dissolution/corrosion mechanisms of alloys and coatings in molten salt or under deposit environments.

Applications, Engineering Achievements and Technology Transfer

The majority of the research performed has a fundamental character. The main applications are to be found in the field of energy conversion (fuel cells) and turbine materials. Part of the work is performed in cooperation with the industry, research institutes, and other universities. The partners are listed in the individual abstracts.

Specific Topics

1. Oxidation of Ni(Cr)Al-Alloys at 1000°C (de Wit, J.H.W.)

This study is performed to understand the parameters influencing the growth rate and adhesion of the scales formed during oxidation of Ni(Cr)Al-alloys at 1000°C. Kinetic data are obtained from gravimetric analysis (TGC), electrochemical experiments, oxidation in ^{18}O containing gases and characterization techniques like Rutherford back scattering (RBS), scanning electron microscopy (SEM) and X-ray diffraction (XRD). It is found that, at 1000°C, K- and L-Al_2O_3 are rapidly converted into P-Al_2O_3, eventually leading to formation of an I-layer. The P-layer grows mainly by outward cation diffusion, which is accompanied by void formation. The growth of the I-layer is determined by anion diffusion, so that the previously formed voids are filled with oxides. As the presence of voids lowers the adhesion, formation of I-Al_2O_3 is preferred. For the Cr-containing alloys it is clearly shown that chromium is present in the scale and that the P<I transformation is accelerated with increasing chromium content in the alloy and probably also in the alloy.

2. Corrosion of Separator Plates of Molten Carbonate Fuel Cells (Hemmes, K. and de Wit, J.H.W.)

The corrosion resistance of materials to be used in molten carbonate fuel cells (MCFC) is studied by exposure tests and by electrochemical methods. The electrochemical experiments are performed in special designed cells in which the composition of the gas environment can be controlled. All experiments are carried out in an eutectic mixture of 62% lithium carbonate and 38% potassium carbonate. In cooperation with the group of Schoonman, Prof. (Section of Inorganic Chemistry, Delft University of Technology), the development and behavior of a coating for the separator plate between cathode and anode compartments in molten carbonate fuel cells. A survey of candidate coatings indicated that only TiN, TiC and Ce-based ceramic seem to be promising. Other coatings are not suited, because they do not have a sufficient corrosion resistance, have a low electronic conductivity, or they do not have a high temperature resistance. The corrosion behavior of stainless steels and nickel-base alloys is studied in cooperation with The Netherlands Energy Research Foundation (ECN). A ranking of the corrosion properties was determined from polarization curves under reducing gas environments. The resistance against corrosion of the alloys increases in the order AISI 316L < Inconel 601 < AISI 310S < Kanthal Al >> Thermax 4762. The order determined from electrochemical experiments is in agreement with the results of exposure tests which are more time-consuming. This study confirms that the presence of large amounts of chromium and significant additions of aluminum have a beneficial effect on the corrosion resistance of stainless steel and nickel-base alloys.

3. High Temperature Corrosion Testing (de Wit, J.H.W.)

In the frame of the Human Capital and Mobility program of the European Union in cooperation with the Max Planck Institute für Eisenforschung, the University of Limerick, UMIST, Research Centre Jülich, ENSC Toulouse, Universita di Genova, IAM/JRC Petten, Universidad Complutense de Madrid and Dechema. Different alloys are studied in an SO_2/air environment with or without a predeposited sulfate layer. Furthermore, the dissolution of alloy constituents in molten sulfate environments is studied in the same manner as described under 2. The scale morphology and composition is studied by SEM/EDX.

4. Interactions Between Glasses and Metals (van der Wijde, D.H. and de Wit, J.H.W.)

This research is financed by, and is performed, in collaboration with Philips. Several practical problems, where oxidation/corrosion of metals due to interaction between glasses and metals at temperatures exceeding 400°C, are studied. Both TGA methods and electrochemical methods are used to study the interactions. It is expected that the results will improve the durability of the components.

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Scientific Key Words: Coating and surface modification; Oxidation/sulfidation; Oxidation as a production route; Fe-Al intermetallics; Spallation

Technical Key Words: Surface engineering; Oxidation/wear resistant coatings; High temperature durable coatings; Oxidation/wear resistant coatings; Waste incineration

SCOPE OF RESEARCH

There are general conflicts between the mechanical properties and high temperature oxidation/corrosion resistance of materials. Engineering alloys working at elevated temperatures and/or in corrosive environments rely on the formation of protective oxide scales such as Al_2O_3 to survive. Bulk corrosion/oxidation resistant alloys often suffer from poor mechanical properties and high cost. Surface coatings and modification are often the best solutions in many practical situations. The new and improved surface technologies studied include unbalanced magnetron sputtering coating, high voltage/high energy surface micro-/nano-crystallisation, and electrochemical deposition. The coating materials are mainly Al-containing alloys or compounds. The applications are concentrated on those used at high temperatures and/or in corrosive environments. Attention is paid to the fundamental problems including the effect of coating microstructure and grain size on the oxidation behaviour, the lowest concentration limits to form a protective oxide scale, the transitions between external and internal oxidation, the generation and release of the stresses in the oxide scales, and the structures and properties of the interface between the coatings and substrates.

Another research direction of this group is to use high-temperature oxidation of alloys as a production route. Controlled oxidation processes have been developed to synthesise oxide mixtures or oxide-metal composites with designed microstructures and properties. High temperature superconductor-silver micro-composites are examples that possess a combination of very good superconducting and mechanical properties. This direction has wide potential application prospects, and is also involved in some of the fundamental studies on oxidation of alloys such as internal oxidation and diffusion behaviors.

This group has a very close relationship with The Centre for Surface and Materials Research, The University of Auckland, where a number of modern surface characterisation and processing equipment are available. The group also has strong research collaborations with the leading research institutions in China including The Centre of Surface Science and Corrosion Engineering, The University of Science and Technology Beijing, and The Institute of Corrosion and Protection of Materials, Chinese Academy. Links with energy, oil, coal, cement, ceramics, metallurgy, pulp & paper, food, and surface coating industries are also being established in the recent years.

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Scientific Key Words:	Mixed gases; Sulfidation; Chloridation; Fatigue/creep evaluation; Remnant life assessment
Technical Key Words:	Coal-fired boiler; Waste-fired boiler; Methanation; Pressure vessel alloys; Petrochemical industry; Deep geothermal

SCOPE OF RESEARCH

Fundamental Approach

The principal goal of the program is the extension of life of industrial plant beyond design life and reducing plant life cycle costs through better availability and reliability. The programme aims to develop new or refined scientific models, and novel data analysis or condition monitoring techniques. The goal is achieved by research into damage accumulation mechanisms and the integration of models of damage accumulation and improved methods of plant condition assessment. The work is focused on providing underlying knowledge and competencies to implement life extension technologies in specific processing industries or infrastructure services. Specific objectives address high temperature corrosion in H_2S- and HCl-containing environments, the use of on-line electrical resistance monitors for high-temperature corrosion and the long-term combined action of creep and fatigue loading. New Zealand and International collaboration in the project planning and execution provides additional scope for technology transfer and accelerated progress through research task sharing. Collaborators include Chemical and Materials Engineering Department, University of Auckland, New Zealand, Tohoku National Industrial Research Institute, Japan, Institute of Geological and Nuclear Sciences, New Zealand, Rohrback Cosasco, USA, ERA Technologies, UK, Electricity Corporation of New Zealand, ANSTO, Australia, Herman Research Laboratories, Australia, Pacific Power, Australia and ESB, Ireland

Applications, Engineering Achievements and Technology Transfer

The work is concentrated on practical industrial problems where existing solutions are inadequate or poorly understood. Extension of the research for applications where economic solutions have not been defined is under way. The principal industry applications are in energy production and petrochemical plant. The following abstracts highlight specific areas of research and testing:

Specific Topics

1. High-Temperature Corrosion

The research objective is to characterise and model corrosion mechanisms which limit the useful life of alloys operated at temperatures above 300°C in process and flue gas environments, in power generation and energy recovery systems, in order to extend plant life by:

- defining the influence of contaminant gas mixtures containing H_2S and HCl under reducing and oxidising conditions over the temperature range 400 to 700°C;
- identifying the reaction mechanisms which result in accelerated 'breakaway' corrosion in the presence of molten salt mixtures, formed for example from metal chlorides and sodium salts under ash deposits, which can flux normally protective oxides.

The objective is aimed at addressing materials problems in existing and future New Zealand energy developments utilising coal, natural gas, landfill gas, biomass gas and geothermal energy reserves.

Specific tasks within this objective are:

- to determine kinetic parameters and corrosion mechanisms of engineering alloys as a function of gas composition and/or molten salt composition;
- to explore corrosion mechanisms in high temperature volcanic environments where corrosive gas mixtures of H_2S, SO_2, HCl and HF are encountered - in collaboration with Tohoku National Industrial Research Institute, Japan and Institute of Geological and Nuclear Sciences, New Zealand;
- to develop a retrievable high-temperature probe capable of simulating the effect of cyclic stress;
- to develop new metal aluminide intermetallics for resistance to high temperature cyclic oxidation.

Work to date has concentrated on development of new models for protective film formation in H_2S-containing environments. In mixed gaseous environments containing

H_2S, HCl and HF encountered in volcanic environments, additions of Mo, Ni, W and Co appear beneficial while Al, Si and Cr and possibly Fe have detrimental effects on corrosion kinetics. High temperature on-line electrical resistance probes developed in collaboration with Rohrback-Cosasco have been demonstrated as suitable for surface corrosion monitoring in steam at temperatures up to 600°C. Additions of Y, Zr and Si to FeAl intermetallic materials have been shown capable of improving cyclic oxidation resistance of these alloys.

2. Creep-Fatigue Life Prediction

The research objective is to specify a validated predictive assessment route for materials and components experiencing the long-term, combined action of creep and fatigue loading in order to optimise and predict the remaining life of capital- intensive, high-temperature, industrial plant, such as thermal power stations and petrochemical furnaces by:

- deriving constitutive mechanistic relationships describing the uniaxial creep, fatigue and stress relaxation behaviour of modified HP50, Durehete 1055, 2.25Cr1Mo and 0.5Cr0.5Mo0.25V high temperature alloys using measurable microstructural and material properties;
- quantifying the effect of extended thermal exposure due to service on creep-fatigue and stress relaxation life of modified HP50, Durehete 1055, 2.25Cr1Mo and 0.5Cr0.5Mo0.25V alloys;
- establishing constitutive mechanistic laws for the description of creep-fatigue performance in ex-service and repair weldments in low alloy ferritic steels, based on the material condition and properties of individual weldment zones;
- specifying a multiaxial stress, creep rupture assessment methodology for Durehete 1055 and 2.25Cr1Mo, based on a simplified novel notched specimen test route;
- specifying and demonstrating novel non-destructive material interrogative techniques to quantify parameters necessary to calibrate the predictive models developed to describe creep-fatigue;
- stating a provisional methodology for the predictive assessment of materials operating under conditions of creep-fatigue.

The methodology will be validated by conducting simulation tests designed to reproduce typical service conditions using a model component fabricated from a current and new generation material. This task will be realised jointly with Industrial Research Limited's collaborative partners and will allow the final specification for the predictive methodology to be stated.

Progress has resulted in the creep-fatigue damage evolution mechanisms in D1055 and 0.5Cr0.5Mo0.25V being related to initial material state and cyclic stress/strain response.

This information has been used as input to an energy based model for life prediction. A semi-mechanistic model relating the results of small punch tests to material toughness has been tested. The low-cycle fatigue performance of the coarse-grained, heat-affected zone, intercritically annealed zone, and parent material has been determined. Data from cross weld specimens containing all these microstructural zones have also been established. These data have been used to develop a predictive model of weldment behaviour based on the properties of the individual zones. A provisional life prediction methodology has been proposed utilising a miniature, multiple step single specimen creep fatigue life prediction model.

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Scientific Key Words: Chromia-forming alloys; Water vapor; Aluminides; Carburization; Thermal barrier coatings; Copper alloys; Defect-dependent properties of oxides

Technical Key Words: Interconnects in SOFCs; Gas turbines; Thermal cracking of natural gas

SCOPE OF RESEARCH

Fundamental Approach

Most of the studies comprise research for master's and doctor's degrees (cand.scient. and dr.scient degrees) and focus on fundamental aspects of high temperature corrosion, with special emphasis on understanding transport processes during corrosion and elucidating reaction mechanisms. Of special interest for many years has been effects of water vapor on the morphology and growth of oxide scales. These effects are particularly evident in high temperature corrosion of various chromia-forming steels; they oxidize faster in humid atmospheres and under these conditions the chromia scales lose protective properties. In parallel with the oxidation studies, the effects of water vapor on defect-dependent properties and the formation of hydrogen defects in oxides are being investigated.

Applications, Engineering Achievements and Technology Transfer

Most of the fundamental studies are related to problems in applications. Thus the studies of the effects of water vapor are, for instance, closely related to the possible use of chromia-forming alloys as interconnects in solid oxide fuel cells (SOFCs); in these the water vapor pressure in the anode chamber will reach high levels. The carburization studies have been related to problems of materials degradation in thermal crackers producing ethylene. The studies of thermal barrier coatings have been part of a BRITE-EURAM project for developing improved materials for gas turbines.

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Scientific Key Words: Air oxidation; Reaction kinetics; Oxide scale morphology

Technical Key Words: Superalloy applications

SCOPE OF RESEARCH

Fundamental Approach

The high-temperature capability and strength of materials generally increase with increasing chromium content and addition of other alloying elements. Addition of many elements in commercial alloys has also increased the complexity of their reaction mechanism. Their oxidation kinetics and reaction products change with temperature and elapsed time of reaction. Since the mechanism of oxidation and oxidation kinetics of commercial alloys are usually partially understood, a detailed comparative study was planned to investigate the oxidation behaviour and mechanism etc. of some superalloys.

Applications, Engineering Achievements and Technology Transfer

There is an ever-increasing demand for better understanding of materials which can withstand the requirements of high temperatures and more aggressive environments in power stations, industrial furnaces, chemical plants, boilers, automobile industries and nuclear reactors. The understanding of the oxidation behaviour of superalloys entails determining the safe application limits and direction for future selection. The main interest of our work has been to study the influence of elements present in some commercially available superalloys on their oxidation resistance in specific environments which are usually encountered in industry at high temperatures. The studies have covered a wide range of temperature (600-1200°C) which could be beneficial with respect to their applications as engineering materials.

Specific Topics

1. *Comparison of Oxidation Behavior of Some High Temperature Alloys (Superalloys) in Air and Steam*

This research is being carried out with the collaboration of PINSTECH, University of the Punjab, Institute of Chemical Engineering and Technology and GIK Institute of Engineering. The aim of the work is to acquire practical knowledge of oxidation behavior of high-temperature alloys (superalloys). Initially, attention was paid to chromium content in increasing order for the seven alloys studied. It was observed that it was not strictly true beyond a threshold value of 12% chromium. However, some of the minor alloying elements play an important role in altering the high temperature oxidation behaviour. The nickel to iron ratio was also considered. Catastrophic oxidation was possibly attributed to a higher manganese content. Similarly, the role of Al, Ti and Mo has been studied. The results of these studies have helped to understand the practical limitations of these materials and upgrading the basic and applied knowledge of the group of metallurgical and chemical engineers involved, on the basis of first-hand information. Such group work helps in the technology-transfer process and understanding materials problems of the local industry. The fundamental aspect of this work include; reaction kinetics, mechanism of oxidation, identification of corrosion products and morphology of oxide scales.

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Scientific Key Words: Crystallography; Deposits; Electron beam surface melting; Erosion corrosion of coatings; Fatigue; Gas-solid reaction kinetics; Impurities; Intermetallics; Lifetime; Microstructural analysis; Modifications; Pollution in air; Surface alloying; Surface modifications; Thermochemistry

Technical Key Words: Aero-engines; Distress in turbines; Electron beam; Sand

SCOPE OF RESEARCH

General Approaches

Electron Beam Surface Melting

The intriguing phenomenon created by the short duration interaction of high energy beams with metals and alloys opens exciting new avenues for the fundamental and technological investigations. Of basic importance in electron beam surface melting are transport phenomena, namely heat flow and fluid flow. The effect of these parameters on the microstructural features and the enhancement in engineering properties is being studied. The microstructural features, chemical composition and crystallography of the phases are being studied using state-of-the-art metallurgical techniques.

The thrust had been on projects of interest from the applications point of view. Work has been done in the synthesis of hard coatings on steels and non-ferrous alloys and the development of texture in EB melted thin surface layers. Innovative results include formation of $M_{23}C_6$ carbides unusually rich in chromium in a high speed steel, elimination of undesirable Al_4C_3 phase in EB rapidly solidified Al- graphite composite material and a wide spectrum of work on surface alloying of materials. The latter includes synthesis of unusually hard surface coatings of aluminum bronze on pure aluminum, formation of Ni_5Al_3 phase with unusual rapidity, modification of surface chemistry of high strength maraging steels. Tungsten alloying of carburized mild steel surfaces has been shown to form carbide phases which are different from those predicted by the phase diagrams.

Another project of interest, both from fundamental and applications point of view, is the rapidity of solid state transformations in the rapidly solidified materials. It has been observed that in rapidly solidified materials the decomposition of martensite is at a rate 2-3 orders of magnitude faster than that occurring during conventional thermal treatment.

Failures in Gas Turbines in Desert Conditions

The research is directed to study the reasons for premature failures in jet turbine aero-engines operating in a desert environment. It is expected that the study will propose the mechanism of failure. The aspects being considered for the study includes hot corrosion in the presence of oxides, silicates in the in-take air and subsequent thermo-mechanical fatigue where the cracks would initiate from the oxidized surface layer. The secondary effects of the hot corrosion include formation of scale on the inside surfaces of the air-cooled turbine blades and vanes and deterioration of the cooling efficiency of the components. An important aspect of the study is the effect of different sands on the high temperature coatings. For this purpose, sand has been collected from different locations in Pakistan. Keeping in view the chemistry of the combustion products in the engine, in sets of experiments the chemical composition of the sand has been modified. Initial results show a significant effect of sand chemistry on hot corrosion.

Corrosion of Various Materials in UF_6 Environments

Work is in progress to study the corrosion resistance of various materials in a UF_6 environment at ambient as well as elevated temperatures. The corrosion resistance of protective coatings is also being examined.

Applications, Engineering Achievements and Technology Transfer

i. Electron Beam Surface Melting

The electron beam technique is very versatile. A very wide variety of compositions can be synthesized on the surfaces of inexpensive materials. Potential applications can include all the surface-sensitive uses.

ii. Failures in Gas Turbines in Desert Conditions

The study was initiated as a result of repeated air accidents. Initial findings concluded that the turbine hardware in general experiences unusual distress. An important application would be in the turbines for power generation whose number in Pakistan is being increased distinctly. The research is in collaboration with Pakistan Air Force.

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Scientific Key Words:	Sulfidation; Refractory metals; Refractory alloys intermetallics; Mechanisms; Point defects; Diffusion
Technical Key Words:	Sulfide and oxide corrosion of refractory metals and alloys

SCOPE OF RESEARCH

Fundamental Approach

The main goal of the research focus is on the kinetics and mechanism of high temperature sulfidation and the oxidation of refractory metals and alloys, as well as on selected intermetallic compounds. In particular, the sulfidation behavior of Mo, Nb and W has been studied as a function of temperature (1073-1273 K) and sulfur activity (10^{-3}-10^{4} Pa) using microthermogravimetric, XRD, SEM, EDS and TEM techniques. Special attention has been paid to various marker methods, including use of the radioactive isotope of sulfur, ^{35}S.

In recent years extensive research programs have been established between this Department and The Institute of Materials Research, Tohoku University, Japan, in order to study the high temperature sulfidation and oxidation behavior of sputter deposited Al-Mo, Al-Nb and Al-Mo-Si alloys. Interesting results have already been obtained (see list of papers no. 1-3,9,11, 13-15, 17-19, 22, 24-27, 29).

In cooperation with the Max-Planck-Institut für Metallforschung, Stuttgart, Germany, CNRS (Laboratoire de Recherches sur la Réactivité des Solides), Dijon, France and

Tokyo Institute of Technology, Japan, extensive research has been initiated to study in details the microstructure, pesting phenomena and corrosion behavior of Mo_3Al_8, Mo_3Al, $MoSi_2$ and $Mo(SiAl)_2$ intermetallic materials in oxidizing gaseous environments. The influence of chromium addition on sulfidation behavior of Ni-Al intermetallic has also been studied.

Other developments include extensive study of thermodynamics and kinetics of point defects in selected metal sulfides. In particular, chemical and self-diffusion in MoS_2 and MnS has been investigated.

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Scientific Key Words: Sulfidation; Oxidation; Coatings; Ceramics corrosion

SCOPE OF RESEARCH

At the Institute of Inorganic Chemistry and Technology at the Kracow University of Technology there is a small group engaged in the study of high temperature processes. The main object of interest of is high temperature corrosion, particularly sulfidation, oxidation and carburization of metals, alloys and ceramic materials. Some work is also often undertaken in conjunction with industrial partners, but this type of work concerns rather wet corrosion.

The objectives of the present research comprise the following topics:

- Corrosion behaviour of intermetallics.
- Fundamental studies; self-diffusion.
- Steam oxidation of metals and ceramics.

The first topic includes the determination of the corrosion properties of thermal barrier coatings in H_2/H_2S gas mixtures and SO_2+O_2 gas mixtures. The research work should contribute significantly to the description and understanding of the corrosion and interdiffusion processes, which occur in coatings at elevated working temperatures. The innovation consists in using a coating technology with consideration given to the economic aspect of material selection and the coating quality and optimising the process parameters and selection of coating material for the substrates applied in turbine blades. The results should contribute to the development of coating technology and improve the corrosion resistance of the components.

The second topic includes fundamental studies on the mechanism of the corrosion of pure metals and double alloys in H_2/H_2S gas mixtures. The studies were carried out, among other things, by means of Mössbauer spectroscopy. The transport properties of the transition metal sulfides were also investigated.

Specific Topics

1. Corrosion Behavior of Intermetallics, such as NiCrAlY Alloys and ZrO_2 + Y_2O_3 in Sulfur-Containing Atmosphere

Sulfidation of alloys having a nominal composition Ni23Co19Cr12Al, with and without the addition of 0.6% yttrium, and Ni22Cr10AlY were studied at the temperatures of 1173 and 1273 K and a sulfur vapor pressure of 10^{-3} - 10^{5} Pa. The sulfidation run was followed thermogravimetrically. Phase and chemical composition of the sulfide scale and scale morphologies were analyzed after different time intervals. The sulfidation of the alloys proceeded at comparable rates. The sulfide scale showed complex microstructure and compositions with several sulfospinel phases present and distinct stratification after longer reaction times. There was no evidence of yttrium segregation either to the grain boundary regions in the scale or to the alloy/scale interface. Yttrium dissolution in the sulfide phases (doping effect) distinctly affected microstructure. Ceramic coatings (ZrO_2+Y_2O_3) corroded in sulfur-bearing atmospheres.

2. Fundamental Studies, Self-Diffusion

The influence of sulfidation on the metallic phase in a series of $Fe_{100-x}Cr_x$ alloys ($x \leq 15$) was investigated by means of ^{57}Fe Mössbauer spectroscopy. The results obtained gave evidence that the sulfidation at 1073 K is selective in the atmosphere of H_2/H_2S with the partial pressure of sulfur ranging from 10^{-2} - 10^{-4} Pa. At x_{Cr} = 5.0 at%, a change of the sulfidation preference occurs.

The diffusion of ^{63}Ni in polycrystalline samples of β-$Ni_{3\pm y}S_{2\pm x}$ has been studied by serial sectioning technique and by fotometering of autoradiographs. The self-diffusion coefficient has been determined as a function of temperature and sulfur vapour pressure at temperatures ranging from 863 K to 943 K and sulfur pressure $3.2 \cdot 10^{-4}$ Pa - 10^{-2} Pa. In these experimental conditions surface, highly diffusive path and bulk diffusion of nickel take place.

3. Steam Oxidation of Metals and Ceramics

As annealed Si_3N_4+1.5% MgO containing a crystalline β-Si_3N_4 phase and intergranular glassy Mg phase was oxidised in water vapour at temperatures 1073, 1173 and 1273 K. The phase stability in the studied system was determined by means of thermodynamic computations. Kinetics of the oxidation were determined by the method of discontinuous measurements of sample mass gain. SEM, EDX and X-ray studies were applied for the original material and the one after oxidation.

The oxidation of Si_3N_4 in water vapour follows the parabolic rate law over a wide range of the exposure periods. Small deviations from this law were detected at the initial stages of oxidation at 1273 K. The apparent activation energy, equal to 148.5 kJ/mole, was determined from the Arrhenius plot. It was found that the scale formed was compact, practically over all its cross-section. However, between the scale and the matrix one could see cracks and gaps. The outer surface of the scale was not smooth; on the surface of the formed layer small craters and pits were observed. It was found, as well, that the outer layer of the scale contained MgO which was practically absent in the scale layer adhering to the matrix.

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Scientific Key Words:	Erosion; Corrosion; Life prediction; Monitoring; Magnetite
Technical Key Words:	Fossil fuel-fired boiler; Furnace wall corrosion; Steam boiler; Coal-fired boiler

SCOPE OF THE RESEARCH

Fundamental Approach

The thrust of the research is to collect and discuss recent advances in methods for on-line and off-line analysis and life prediction of boiler tubes. Accurate high temperature metrology methods are now available giving significant measurements in a much shorter time than in the past. On-line corrosion and erosion monitors are being developed which give a significant response in periods of hours and days. Thin layer activation is now being transferred from laboratory to power plant for erosion measuring. Off-line monitoring by ultrasonics allows accurate measurements of steam-side oxidation growth and is being a significant tool to estimate average temperature, allowing anticipation of components' behavior. Wastage in boiler tubes and corroded defective areas can be visualised by LASER shearography methods. This new NDT technique can cover large areas rapidly and provides visualization of real time defect images related to abnormal condition in the structure when it is under stress. The work done includes the context of its application and feasibility for inspection in water wall and superheater and reheater tubes of boiler furnaces.

Applications, Engineering Achievements and Technology Transfer

In this work recent advances in methods of measuring tube temperature, corrosion and erosion rates in boiler tubes have been discussed. These are all factors which affect the life of tubes and better measurements will allow more accurate life prediction. Thermocouples can provide tube temperature measurements but they are short lived in aggressive environments and costly. There is a range of techniques in different stages of development, which allow an effective average temperature between outages to be accessed, each dependent on a different diffusion controlled process. Steam side oxidation is temperature dependent. Its accurate measurement can be used for off-line monitoring the temperature of steam cooled boiler tubes. These techniques can provide improved life prediction, since their response is determined by the entire thermal history during a campaign. A major advance in the last few years has been the development of on-line high temperature corrosion monitors. These techniques should allow the effects of operating variables on corrosion rates to be determined, because they give a significant response in periods of hours or days, rather than the months in conventional tube wall thickness measurements. The work has been undertaken in conjunction with industrial partners.

The group has been involved with others in considering the relative merits of different approaches and these are described in the references listed here, emerging from these groups.

Specific Topics

1. Effective Temperature Monitoring

The aggressive environments, encountered in industrial plant, make thermocouples short-lived and costly methods of measuring temperatures. Efforts have been made to develop techniques which can be reliably used to measure temperature. None of the techniques under development for measuring temperatures, reliably and over extended periods, (e.g. between plant outages), gives an instantaneous indication of temperature but, instead, gives an effective average temperature, which takes into account temperature fluctuations over the duration of the exposure. The effective temperature required for input into life predictive techniques is that which would produce the same amount of damage (e.g. by creep corrosion). Various temperature measurement systems are available and are described below. With each of these techniques, a material change is measured which depends on diffusion and is therefore time- and temperature-controlled. Consequently, with a knowledge of the diffusion kinetics and the duration of exposure, a temperature can be determined. Under isothermal conditions, the temperature determined will be the effective temperature of the damage processes; however, where the temperature is varying the temperature determined will generally be slightly different from the effective temperature of the damage processes. This is due to the inevitably different temperature dependence of the effects and has been covered in more detail by Westwood et al. (See reference list).

1.1 Diffusion Controlled Methods

This approach involves use of a bimetallic diffusion couple encased in an oxidation resistant sheath. Proprietary versions are available. These capsules can be installed on plant during a convenient outage and exposed to elevated temperatures. At the next outage the capsule is removed and the radial diffusion profile is analyzed using quantitative energy dispersive X-ray analysis on a scanning electron microscope. The effective temperature is determined from the diffusion profile using a proprietary software package. Various approaches for attachment of the device have been developed and are described in the references by Meadowcroft et al.

In other devices, available commercially, the amount of ferrite after ageing, for long periods (the order of 5000 hours), is characteristic of the temperature of exposure. Again the method of attachment is imported. As yet, however, it is not clear how the sensors correspond to cyclic temperature conditions and what effective temperature they will indicate. A current study aims to investigate this and to determine calibration curves for several different duplex alloys.

1.2 Steam Side Oxidation Measurements

Steam side oxidation is a temperature controlled process so its progress can be used to monitor the temperature of steam cooled boiler tubes. In ferritic steam superheater tubes (e.g. 2 1/4 Cr) the oxide thickness is a unique function of of the temperature and time of exposure. This can be measured non-destructively on the internal surface of boiler tubes using advanced ultrasonic methods. Over recent years a considerable amount of work has been carried out in the USA under the auspices of EPRI and in Europe under SPRINT and BRITE EURAM programs, where ISQ has a strong participation . This has been assessed in the references cited (e.g. Borros et al., and by Adkins and Sherlock).

The major difficulty arises because the steam side oxidation behavior of low alloy steels is not simple and the rates of corrosion can vary widely depending on whether the oxide is growing in a 'duplex' or 'multi-laminated' form (Grobner). In any ISQ assessment of component integrity by this method, complementary metallographic sections are examined, in order to ensure that the oxide growth law applied is correct for that particular oxide morphology.

2. High Temperature Erosion/Corrosion Monitoring

2.1 Off-Line Methods

2.1.1 Laser Shearography

Location of intensive eroded/corroded areas in boiler tubes are generally detected and measured by ultrasonics thickness measurement. A preliminary inspection grid is established and the data obtained could be organised in historical data records. The main problem consists of restricted information concerning local wastage or pitting corroded areas. ISQ is currently leading the development of LASER Shearography technique on tube wall furnaces as well as superheater and reheater pendants, using commercially available equipment. This new NDT technique, non-invasive and accurate, can cover large areas and provides visualization of real time defects images related to abnormal condition in the structure when it is under stress. First documents relating to this particular application in water wall tubing are publicized in USA, by Bobo in 1991, Following development and validation in the laboratory, using mock-up arrangements made from used (ex-service) tubes, the method was successfully applied in power plants in Portugal and Spain. As with ultrasonics, this is an off-line monitoring technique, but the data and information obtained is larger. Ultrasonic thickness measurement's reliability is surface-condition dependent. Defects such as pitting and cracking require elaborate and time-consuming procedures. LASER shearography showed good detectability for internal pitting allowing the detection of diameter 2 mm by less than 0.5 mm depth pitting, (10% of nominal thickness). This is described in the paper by Tyson. The paper by Barata should also be considered.

2.2 On-Line Methods

2.2.1 Corrosion Monitoring

On-line monitors for low temperature corrosion have been available for many years now. These measure electrical signals continuously which relate to metal loss rate. Two of the 'low temperature' methods have recently been redesigned to work at high temperatures. In one method, electromechanical properties are measured, while in the other the increase in electrical resistance as the electrode wastes is measured. Both techniques are still under commercial development by several vendors, and there is a need for independent validation of their capabilities. Electrical corrosion monitors offer distinct advantages over direct measurements of thickness loss on exposed materials. The corrosion rate information is available very quickly and, by applying an appropriate integration period to the data, the change in corrosion rate with changes in operation conditions can be determined, allowing optimization of operating parameters to minimize corrosion effects. However, much effort has been needed in their development. In high temperature plant the corroding materials often operate in a heat flux; consequently, reliable and effective cooling methods are required for the probe elements to achieve heat transfer conditions, a requirement not present in low temperature applications. Accurate measurement of surface metal temperature achieved is also necessary, to keep the surface temperature constant and to be able to relate corrosion rate to temperature. Electrochemical effects, involving surface deposits, which play an active role in high temperature corrosion process are used in one monitoring technique. The techniques used are the same as in low temperature applications, including impedance, zero resistance ammetry, and potential and current noise (see the paper by Simms). In appropriate environments, this technique give responses which enable wastage rate and a type of corrosion (uniform or pitting) to be estimated over a matter of hours, and hence once properly validated will be invaluable for determining the effects of operating conditions on corrosion in an operational plant. The electrical resistance method relies on measurements of the increase in resistance of a metal electrode as it thins through corrosion. As metal resistance changes with temperature the difference in resistance from a reference electrode protected from the environment but at the same temperature, is generally determined to provide a calibration. To overcome the difficulties in high temperature the probe must be generally cooled. This technique is more direct than electrochemical probe, but the later can potentially obtain indications of corrosion rate more rapidly.

2.2.2 Erosion Monitoring

Thin layer activation has been used to monitor wear and erosion processes in laboratory for some years now. The technique requires that a thin layer at the surface of the component is activated with a low level of radioactivity. When material from the layer is lost there is a consequent loss of radioactivity detectable and the thickness of material loss can be determined. Activation is carried out in an accelerator, where elements within the component surface are converted to radioactive isotopes when they are bombarded by high energy charged particles. The depth of activation is determined by the energy of the particles and the level of activation by the duration of bombardment. When radioactive isotopes decay, gamma radiation is emitted and this can be detected remotely, even through the boiler casing, up to a total distance of about 1.3 m. The level of radiation detected is reduced through natural radioactive decay (determined by half life of the isotope) and through material loss. For continuous measurements the natural decay of the isotope can be built into the analysis system but, for discrete readings, it is better to compare measurements with a calibration sample, activated at the same time and with the same isotope as the component surface. Gamma radiation is highly penetrating, allowing measurements to be taken at some distance and through solid objects. Limitations of the technique are described in the publications listed. In a current EC project the technique was applied in a power station boiler to monitor erosion of economiser tubes. This has required the development of working practices and safety procedures to make the technique acceptable for routine plant applications.

3. Conclusions

Improvements in the ability to predict the life-time of high temperature components have occurred in the last few years. Several techniques are now available or under development; they are suitable for 'effective' temperature experienced in service conditions. Innovative and accurate non-destructive methods, such as LASER shearography, have been validated for defect assessment and erosion and corrosion off-line evaluation; accurate steam side oxidation measurements by ultrasonics, allowing correlation with operating temperature, are a reliable tool for boiler components life prediction. On-line corrosion sensors are under development using resistance or electrochemical techniques; the time scale provided in estimating corrosion rates allows its optimisation by changing operating conditions. Thin layer activation to measure erosion rates on-line has been successfully used on an operating power plant to monitor economiser erosion rates. This required the development of safe working practices suitable for an industrial environment.

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SPAIN

CONTENTS

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Scientific Key Words: Void formation during oxidation; ODS alloys; Intermetallics; Ion implantation; Alumina; Preoxidation; Residual stress; Stresses and scale behavior; Adherence

SCOPE OF RESEARCH

Fundamental Approach

Specific Topics

1. Void Formation During Oxidation

The phenomenon of void formation during high-temperature oxidation has been studied for the ODS alloy MA 6000. The effect that results from oxidation was analyzed for stress-free and stressed samples exposed to creep deformation up to a maximum exposure time of about 11000 hours at 1050°C. Additional tests in the stress-free condition have been performed at 1150°C for up to about 1300 hours. This work was undertaken at the Institute for Advanced Materials of the Joint Research Center, at Petten Establishment (The Netherlands).

2. Ni-Based Intermetallics

The most recent work on high-temperature oxidation relates to studies on the oxidation behavior of Ni_3Al processed via Powder Metallurgy in the laboratory. The oxidation behavior has been investigated in the temperature range of 530°C to 1020°C for exposures of up to about 150 hr by means of discontinuous isothermal tests. Emphasis was devoted to investigate the low-high temperature transition mechanism. The effect of the powder particle size used for the preparation of the compact on the oxidation kinetics has also been investigated. This work has been performed as a part of the doctoral thesis of Pérez, P., on the "Mechanical Characterization and Oxidation Behavior of Ni_3Al Processed by Powder Metallurgy". Besides there has been initiated a collaboration with Stroosnijder, R., Dr. (Institute for Advanced Materials of the Joint Research Center, Ispra Establishment) to investigate the effect of ion implantation (Cr, Y) on the oxidation behavior under cyclic and isothermal conditions. At present most of the results are under evaluation and unsettled for open publications.

3. MA 956

The research includes fundamental studies of the effects of the alumina scale and cooling conditions on the room-temperature behavior of preoxidized MA 956 in the strain-rate range of 10^{-5} to $10^{-1}s^{-1}$. It has been found that the yield strength and the tensile strength are lowered with respect to those of the scale-free material. From the analysis of the differences, residual compressive stresses in the scale of about 5500 MPa were obtained. Besides, the scale increased the triaxiality state in the substrate, decreasing the ductile-brittle transition strain rate at room temperature. For the slower cooling condition, an increase of the yield strength, associated to a precipitation at intermediate temperatures of a metallic phase, was found. On the other hand, a study of the role of the surface roughness has been carried out on the thermal stress distribution in the scale. A fracture mechanics analysis, aimed to explain the brittle behavior of the preoxidized MA 956, has been also performed. Other studies include texture analysis as a function of the processing conditions. Oxidation experiments and electrochemical tests, aimed to evaluate the integrity of the scale, are part of the Doctoral Thesis of García-Alonso, C., about the "Characterization of Preoxidized MA 956 as a New Biomaterial". Most of the present results have been submitted to scientific journal and they are not completed for open publications.

Applications, Engineering Achievements and Technology Transfer

The ODS MA 956 alloy is widely used at high-temperature because its unique capability to develop a dense, fine, and adherent α-alumina scale. For applications at low temperatures or under low oxygen partial pressure, where formation of the scale is precluded, the fabricant recommends a preoxidation treatment. In the laboratory a novel application of preoxidized MA 956 superalloy for surgical implants is being investigated. The proposal is based in the excellent *in vitro* and *in vivo* behavior of the α-alumina against the aggressive action of organic fluids. Since the information on the room temperature behavior is scarce, a wide investigation about the effect of the preoxidation treatment on the mechanical properties (tensile properties, texture, fatigue, wear, etc) has been undertaken at room temperature. Due to great technological interest of this alloy results emerging from this investigation are also of interest for other applications.

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Scientific Key Words: Coatings; Chemical vapor deposition; Electrochemical methods; Hot corrosion; Ion implantation; Molten salts; Oxidation; Surface engineering

Technical Key Words: Municipal waste-burning; Waste incineration; Heat exchangers; Aeroengines; Engine materials; Condensate corrosion

SCOPE OF RESEARCH

Fundamental Approach

The thrust of the research is on the role of the studies of different high temperature corrosion problems of metals and alloys, including their protection by coatings. Emphasis is on the analysis of corrosion mechanisms, oxidized layers growth and protective properties. The research includes fundamental studies in the development of new coating systems in different industrial applications in the power generation industry. Examples of these applications include gas turbine environments and waste incinerators where molten salts may be deposit. The research is complete at this time with a corrosion test in gaseous atmospheres, simulating combustion systems and waste incinerator atmospheres. This research is performed with another research groups in Europe under the TMR program, and in the USA with the SRI-International Research Center.

Applications, Engineering Achievements and Technology Transfer

The most important present achievement is in the development of monitoring systems to perform corrosion surveillance of waste incinerators plants, in the hot corrosion processes due to molten chlorides that are being deposited in these atmospheres. The national industry is very interested in this R&D field. Otherwise, the development of a coating system by CVD in FBR is very attractive for different industrial applications, for the composites industry, and for the aerospace industry.

Specific Topics

1. Hot Corrosion in Molten Salts in Waste Incinerator Environments: Molten Chlorides

This research is being carried out in collaboration with nine research groups in Europe under a Human Capital and Mobility programme grant. The overall aim of this work, concerning the research group is to develop an electrochemical system to perform the test long enough to define the kinetics of the corrosion processes. Moreover, Electrochemical Impedance Spectroscopy (EIS) experiments are being carried out in order to define the corrosion mechanism under molten deposits, and to design materials and coatings to resist this kind of aggressive environment. Another purpose in applying this technique is to develop in the future the application of EIS to corrosion monitoring below molten deposits.

2. Corrosion of Materials Under Sulfidizing/Oxidizing Conditions in Industrial Processes

This work is being carried out with the Spanish Research Foundation, in order to define the extension and nature of these corrosion processes in the national power generation industry, to analyze the life remaining of the plants and the possibility to design new materials and coatings for this kind of application. Emphasis is placed on the influence of sulfur in low oxygen-containing gases on this kind of high temperature corrosion process.

3. Thermal Barrier Coatings for Aerospace Applications

This research is performed with the National Aerospace Institute (INTA), working in the develop of new ‘non-ceramic’ thermal barrier coatings for industrial applications. This collaboration between the institutions aims to develop the technology to provide the coating and blade repair for the military industry.

4. Development of Different Coatings by CVD-FBR

Different diffusion coatings are being applied on various superalloys and steels for high temperature applications. The advantages of the CVD-FBR technique are clear as these coatings perform in better conditions than other possible coatings techniques. This research is performed jointly with the SRI-International (California. USA) to provide metallic and non-metallic coatings.

SPONSORS

- North Atlantic Treaty Organization. NATO.
- European Commission. EU.
- Interministerial Commission of Science and Technology. Spain.
- Autonomus Government of Madrid. Spain.
- Acerinox, S.A. Spain.
- ENDESA. Spain.
- FENOSA. Spain.

INTA. National Aerospace Institute.. Spain.NETWORKS

- High Temperature Corrosion and Coatings (TMR)
- UMIST. U.K.
- Aristoteles University of Thessaloniki. Greece.
- Julich Research Center. Germany.
- ANSALDO. Italy.
- Max-Planck-Institut für Eisenforschung. Germany.
- University of Genova. Italy.
- JRC- Institute for Advanced Materials. The Netherlands.
- University of Limerick. Ireland.
- DECHEMA Institut. Germany.

ALPHA Network (European Commission) in Coatings

- University of Thessaloniky. Greece.
- University of Northumbria at Newcastle. U.K.
- Universidad Central de Caracas. Venezuela.

- Universidade de Mogidas Cruzas. Brazil.

DESIRED LINKS OR COLLABORATIONS

In the following research fields:

- High temperature corrosion below molten deposits.
- Coatings for high temperature applications.
- Thermal barriers.

RECENT PUBLICATIONS

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2. Otero, E., Pardo, A., Perez, F.J., Alvarez, J.F. and Utrilla, M.V., "Surface Modification of the IN-657 Superalloy After Exposure to a Molten Mixture: 82%$K_2S_2O_7$-18%V_2O_5 at High Temperature," Surface and Coatings Technology, 68/69, 58-63 (1994).

3. Otero, E., Pardo, A., Perosanz, F.J., Orts, J., Maffiotte, J. and Perez, F.J., "Surface Modification of Several Steels After Their Exposure at High Temperature to Oxygen and Sulfur Mixtures," Surface and Coatings Technology, 76-77, 53-60 (1995).

4. Otero, E., Pardo, A., Perez, F.J., Alvarez, J.F. and Utrilla, M.V., "The Effect of Different Surface Treatments on the Molten Salt Hot Corrosion of IN-657 Superalloy," Surface and Coatings Technology, 85, 156-162 (1996).

5. Otero, E., Pardo, A. Perez, F.J., Alvarez, J.F. and Utrilla, M.V., "A High Temperature Corrosion Kinetic Study of HK-40 Superalloy Surface Treated in Contact With Eutectic Mixture 82%$K_2S_2O_7$-18%V_2O_5," Corrosion Science, 39, 133-145 (1997).

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Scientific Key Words: Nitridation; Carburization; Chloridation; Sulfidation; Steel nitridation; Water; Chromia; Alumina; Cold work effect; Fatigue-oxidation interactions

SCOPE OF RESEARCH

Fundamental Approach

The main emphasis of work to date has been on high temperature phenomena in conjunction with the annealing of stainless steels. During bright annealing the formation of nitrides or a visible surface oxide must be avoided by careful control of the partial pressures of oxygen, nitrogen and water vapour in the system. Research includes surface characterisation with GDOES and TEM, thermodynamic evaluation and kinetic modeling of the interplay between protective and non-protective oxides, nitride formation and nitrogen uptake in solid solution. Conventional annealing in electric or gas/oil fired furnaces produces thick scales which contain oxides of iron, chromium, molybdenum and silicon. The role of water vapour, oxygen partial pressure, secondary phases, cold work and surface contamination has been examined with the ultimate aim of modifying the oxide structure so as to facilitate subsequent pickling operations. A second important area of work is the interaction between mechanical stress and oxidation behaviour. The effect of oxide rupture during simple loading and fatigue testing on oxidation rates is being investigated for steels which form chromia, chromia/spinel and alumina scales.

Applications, Engineering Achievements and Technology Transfer

High temperature corrosion of both chromia and alumina forming steels is being studied in model oxidising/choridating and oxidising/sulfidising environments in order to gain fundamental understanding of complex corrosion process of relevance to combustion systems. Interaction between high temperature corrosion and low cycle fatigue is being investigated in a hydrogen-carbon monoxide environment designed to avoid metal dusting. Current international collaboration is within the frame of European projects on standardisation of high temperature corrosion testing (SMT - Testcorr) and materials for waste incineration environments (ECSC).

RECENT PUBLICATIONS

1. Jargelius-Pettersson, R.F.A., Ekman, T., Hertzman, S., Holm, T. and Linder, J., "Nitrogen Uptake by Austenitic Stainless Steels on Annealing in N_2-H_2 Atmospheres," Materials Science and Technology, 9, 1123-1132 (1993).

2. Jargelius-Pettersson, R.F.A. and Szakalos, P., "Oxidation of Fe-Ni-Cr Alloys in Air at 1100°C," SIMR Report IM-3253 (1995).

3. Jargelius-Pettersson, R.F.A. and Szakalos, P., "Oxidation of Type 304 Stainless Steel During Annealing," Stainless Steels '96, Dusseldorf, 348-349 (1996).

4. Jargelius-Pettersson, R.F.A., "Characterisation of Oxides Formed on Stainless Steels at 800-1100°C," 3rd International Conference on Microscopy of Oxidation, Cambridge (1996).

5. Jargelius-Pettersson, R.F.A. and Szakalos, P., "The Effect of Cold Work, Surface Condition and Oxygen Partial Pressure on the Oxidation of Stainless Steels at 1100°C," SIMR Report IM-3374 (1996).

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Key Personnel:	Chen, J., Dr., Pompe, R., Dr., O´Meara, C., Dr., Svensson, J.-E., Dr., Norell, M., Dr., Olefjord, I., Prof., Leygraf, C., Prof., Herzman, S., Dr., Pettersson, R., Dr., Johansson, L.-G., Dr., Hultqvist, G., Dr.
Scientific Key Words:	Ceramics corrosion; Corrosion-mechanical property interactions; Erosion corrosion; Aluminide coatings; Mixed oxidants with water vapor; Electrochemical characterisation
Technical Key Words:	Ceramic components in gas turbines; Single crystal alloys; Waste incineration in circulating fluidised bed; Fossil fuel-fired boiler; Biomass combustion

SCOPE OF RESEARCH

Fundamental Approach

The High-Temperature Corrosion Centre (HTC) at Chalmers University of Technology, Göteborg, Sweden was started 1 October 1995. HTC is sponsored jointly by industry, the university and by the Swedish National Board for Industrial and Technical Development (NUTEK). HTC represents an effort to concentrate and co-ordinate research on high temperature corrosion in Sweden. The research is carried out in a close collaboration between researchers at the university and in research institutes as well as involving industrial partners. HTC covers fundamental and applied aspects of high temperature corrosion.

Projects

Currently five projects are running:

- High-Temperature Corrosion in Circulating Fluidised Bed Combustion of Municipal Waste.
- Fundamental Aspects of Oxidation and Corrosion in Combustion Environments
- High-Temperature Corrosion and Oxidation of Ceramics.
- Interaction Between Mechanical Load and High-Temperature Corrosion.
- Oxidation of PtAl Diffusion Coatings on Nickel-Base Alloys.

Partners in HTC

At Chalmers University of Technology and University of Göteborg: Inorganic Chemistry, Inorganic Environmental Chemistry, Engineering Metals, Microscopy and Microanalysis, Energy Conversion and Energy Systems Technology, Thermo and Fluid Mechanics

In addition, the following university departments and research institutes take part: Materials Science, Royal Institute of Technology, Inorganic Chemistry, University of Stockholm Institute of Metals, Swedish Ceramic Institute.

Industrial partners: AB Sandvik Steel, Avesta Sheffield AB, Kanthal AB, Kvaerner EnviroPower AB, Volvo Aero Corporation, ABB STAL, Stockholm Energi, Sydkraft, Vattenfall.

Applications, Engineering Achievements and Technology Transfer

Specific Topics

1. *High-Temperature Corrosion in Circulating Fluidised Bed Combustion of Municipal Waste*

This project involves the exposure of 12 different tube materials ranging from carbon steel to 62Ni 22Cr 9Mo (Sandvik 625; compound tube) and including Fe_3Al coated tubes in a commercial CFB boiler fired with 100% refuse-derived fuel (RDF). The object is to study the erosion and corrosion of tubes in the water-wall and superheater region as a function of temperature and position and to compare the performance of the different alloys. The exposure, which lasts for 700 hours, does not involve the insertion of cooled probes into the boiler. Instead the samples make up part of the water-wall and superheater, being connected to separate cooling systems. Corrosion rate is measured gravimetrically as well as by profilometry. The deposits, corrosion products and corrosion product/metal interface will be investigated by a combination of optical microscopy, SEM/EDX, XRD and Auger spectroscopy. Laboratory exposures are also included.

Project leader: Norell, M., Dr., Engineering Metals, CTH.

2. High-Temperature Alloys in Combustion Environments

This project focuses fundamental aspects of the oxidation and corrosion of Fe-Cr alloys. The materials T22(21/4% Cr); X20 (8-12% Cr), 304L (18%Cr 10%Ni) and 310 (25% Cr 20% Ni) are isothermally exposed to synthetic gas mixtures in the laboratory. Part of the project deals with the effect of H_2O(g) on the oxidation behaviour. One main objective is to study the effect of corrosive gases such as SO_2/SO_3 and HCl using temperatures of 500-700°C and the concentration of the corrosive gases in the range 10-1000 ppm.

The surfaces of the corroded samples are characterised by optical microscopy, X-ray diffraction, SEM/EDX, Scanning Auger Microscopy, GDOES and XPS. Impedance spectroscopy is used to characterise the electrochemical properties of the oxide.

Project leader: Svensson, J.-E., Dr., Inorganic Environmental Chemistry, CTH.

3. High-Temperature Corrosion and Oxidation of Ceramics

The object is to study the high temperature corrosion of ceramic materials in environments relevant to combustion processes and changes in mechanical strength/defects related to, or caused by, high temperature corrosion. Until recently the work was directed towards monolithic silicon nitride and composites such as Si_2N_2O/ZrO_2. Samples are exposed in controlled environments in the laboratory, in the temperature range 1000-1600°C, with special attention to the effects of water vapour and NaCl. The corrosion process is studied by TGA, ellipsometry and TEM. Applications are primarily in relation to gas turbine technology. New activities within the project includes work on silicide materials used as heating elements, studying low-temperature pesting and high-temperature corrosion. Work will also be started on the corrosion resistance of ZrO_2 coating on Ni-alloys in the presence of salt.

Project leader: Pompe, R., Dr., Swedish Ceramic Institute.

4. Interaction Between Mechanical Load and High-Temperature Corrosion

This project concerns the interaction of mechanical load and high-temperature corrosion for three different alloys; 304, 253MA and APM. Samples are exposed in a rig designed to study low-cycle fatigue at high temperature in a controlled environment.

The effect of, e.g., O_2, H_2O, H_2, CO, SO_2 and HCl is investigated. The oxide and the oxide/metal interface are studied with respect to microstructure and composition, using microscopy and a combination of surface analytical methods. The project also includes the electrochemical characterisation of oxide scales using impedance spectroscopy at ambient temperature. The object is to improve on the optimisation and assessment of useful life for load-carrying structures in aggressive environments.

Project leader: Herzman, S., Dr., Institute of Metals.

5. *PtAl Diffusion Coatings on Nickel-Base Alloys for Gas Turbines; Effect of Different Factors on the Useful Life of Coatings.*

The project focuses the processes that limit the useful life of Pt/Al coatings on Ni-base alloys. This includes oxidation/corrosion of the coatings as well as the diffusion of aluminium into the base material. The project involves isothermal oxidation exposures of PtAl coatings on single-crystal Ni alloys. The microstructure and composition will be investigated by optical microscopy, SEM, TEM, EDX and EELS (electron energy loss spectroscopy). The object is to contribute to the understanding of the processes that tend to break down the coatings, to improve on the assessment of useful life and to help to create a better specification of requirements for these coatings.

Project leader: Stiller, K., Dr., Microscopy and Microanalysis, CTH/GU.

RECENT PUBLICATIONS

1. Chen, J., Heim, M. and Pompe, R., "Oxidation Kinetics of Silicon Nitride Ceramics: Influence of Crystallisation and Additive Enrichment in the Oxide Scale," 4th International Symposium on High Temperature Corrosion and Protection of Materials, International Journal of Materials Science Forum, in print (1996).

2. Heim, M., Chen, J. and Pompe, R., "Dry and Wet Oxidation of a Si_2N_2O-ZrO_2 Composite Material," Submitted to Journal of Materials Science (1996).

3. Heim, M., Chen, J., O´Meara, C. and Pompe, R., "The Oxidation and Salt Corrosion of a Si_2N_2O-ZrO_2 Composite Material," Ceramic Engineering and Science Proceedings, 17, (4 and 5), in press (1996).

4. Heim, M., Chen. J. and Pompe, R., "Wet and Salt Corrosion of a Si_2N_2O-ZrO_2 Composite Material," Journal of the European Ceramic Society, in press (1996).

5. Heim, M., O´Meara, C., Chen, J., Gatt, R. and Pompe, R., “On the Oxidation Kinetics of a Si_2N_2O-ZrO_2 Composite Material,” Submitted to Journal of the Electrochemical Society (1996).

6. Heim, M., Chen, J. and Pompe, R., “Oxidation, Wet and Salt Corrosion of a Si_2N_2O-ZrO_2 Composite Material,” in Proc. 2nd Int. Meeting of Pacific Rim Ceramic Societies,Cairns, Australia, in press (1996).

7. Nordberg, L.-O., Nygren, M., Käll, P.-O. and Shen, Z., “Stability and Oxidation Properties of RE-a-Sialon Ceramics (RE=Y, Nd, Sm and Yb),” Submitted to Journal of the American Ceramic Society (1996).

8. Pan, J. and Leygraf, C., “Characterisation of High-Temperature Oxide Films on Stainless Steels by Electrochemical Impedance Spectroscopy,” Submitted to Oxidation of Metals (1996).

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Scientific Key Words: Heating elements; Electrical heater materials; Cyclic oxidation; Creep/oxidation; Alumina growth/breakdown; High temperature fatigue; Life assessment

Technical Key Words: Industrial furnaces; Heating elements; Heat exchangers; Gas burners; Waste incineration; Appliances

SCOPE OF RESEARCH

Materials and process development of high temperature materials and systems is undertaken. The most important materials are Ni-Cr-(Fe), Fe-Cr-Al (wrought and PM), SiC, $MoSi_2$, ZrO_2 and high temperature fiber insulation. Evaluation of basic oxidation, high temperature corrosion, creep and fatigue properties, as well as application oriented testing, is undertaken.

APPLICATIONS

Electrical resistance materials, electric and gas heating systems, bimetals, high temperature structural materials, thermal protection and insulation, and coatings are all considered.

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Scientific Key Words: Gas-solid reaction kinetics; Bulk oxide properties; Water; Hydrogen Absorption; Secondary ion mass spectroscopy; Electrochemical measurements

Technical Key Words: Heating elements; Furnace wall corrosion; Catalyst support systems; Zirconium/water/steam

SCOPE OF RESEARCH

Specific Topics

1. *Electrochemical Studies of Oxide Films Formed on Stainless Steels Under High Temperature Corrosion Conditions (Leygraf, C.)*

The aim is to use electrochemical impedance spectroscopy for characterization of oxide films formed on stainless steels under high temperature corrosion conditions. The measurements provide information about electrical properties of the oxide film, which depend on the material and oxidation parameters. The result for three stainless steels have shown that the growth of oxide films, existence of pores/cracks and breakthrough of the films can be evaluated. The observations are in agreement with practical experience. Further investigations of high temperature oxide films are carried out, which form part of a Competence Center for High Temperature Corrosion. The project was initiated in 1995 and no papers have yet been published.

2. *Studies of Reaction Mechanisms and Kinetics in Metal-Oxygen-Water Systems Directed Towards High Temperature Corrosion (Hultquist, G.)*

The aim is to improve the basic knowledge of metal-oxygen-water systems mainly by using Mass Spectrometry and Secondary Ion Mass Spectroscopy in combination with isotopic marked oxygen and hydrogen. Reactions of Al,Cr,Cu,Fe and Si in gas mixtures of $H_2{}^{18}O$, $H_2{}^{16}O$, ${}^{18}O_2$ and ${}^{16}O_2$ in the 10mbar pressure range have been studied in situ with mass spectrometry in a virtually closed chamber. The consumption and release of gas components during the reaction were monitored. When these results were combined with subsequent SIMS analysis of the formed reaction products, hydrogen uptake in the reaction product and the role of molecular oxygen in O_2/H_2O-Me reactions were revealed.

The exchange of oxygen in O_2 molecules, which takes place in contact with various solid samples, has been studied on Pt and different metal oxides. This has been done by the use of ${}^{16,16}O_2$ and ${}^{18,18}O_2$ with a concomitant measurement of ${}^{16,18}O_2$ formation rate. From these experiments it is concluded that all the studied metal oxides act as catalysts for oxygen exchange in molecular oxygen, although at widely different efficiencies. The exchange of O in O_2 molecules can also be the result of oxygen exchange with the metal oxide and efforts are made to relate these phenomena to reaction kinetics in high temperature corrosion.

We also try to gain a better insight into the role of water and hydrogen in the growth of alumina, zirconia and silica by using the experimental methods described above.

RECENT PUBLICATIONS

1. Experimental and Analytical Methodology

1. Lu, Q., Hultquist, G., Tan, K.L. and Åkermark, T., "A Calculation Method for Analysis of SIMS Spectra from Oxidation of Metals in $H_2{}^{16}O/H_2{}^{18}O/{}^{16}O_2$ Gas Mixtures," Surface Interface Analysis, 20, 645-650 (1993).

2. Hultquist, G., Mathieu, H.J., Gopalakrishnan, R., Yones, C. and Lu, Q., "Secondary Ion Mass Spectrometry Analysis of Ion Oxides with Known ${}^{18}O/{}^{16}O$ Contents," Surface Interface Analysis, 21, 800-804 (1994).

3. Åkermark, T., Hultquist, G. and Lu, Q., "Release of Water and Hydrogen During Outgassing of Some Materials," Journal of Materials Engineering and Performance, 5, 516-520 (1996).

2. Initial Reaction, nm Oxide Thickness

4. Lu, Q., "Initial Oxidation of Cr at 300-730K in $H_2{}^{16}O/H_2{}^{18}O/{}^{16}O_2$ Gas Mixtures Studied In-Situ with ^{18}O/SIMS and XPS," Oxidation of Metals, 40, 421-432 (1993).

5. Lu, Q., Hultquist, G. and Gråsjö, L., "A Comparison of the Initial Reaction of Pure Fe, Cr and Al in $H_2{}^{16}O/H_2{}^{18}O/{}^{16}O_2$ Gas Mixtures at 300-730K Studied In-Situ with SIMS," Corrosion Science, 36, 927-939 (1994).

3. Growth of Thick Oxides

6. Hultquist, G., Gråsjö, L. and Lu, Q., "Consumption and Release of Gas Components During the Reaction of Iron at 300°C in a $H_2{}^{16}O/H_2{}^{18}O/{}^{16}O_2$ Gas Mixture," Corrosion Science, 34, 1035-1038 (1993).

7. Hultquist, G., Gråsjö, L., Lu, Q. and Åkermark, T., "The Analysis of Gas Consumption in the Reaction of Fe and Cu in $H_2{}^{16}O/H_2{}^{18}O/{}^{16}O_2$ Gas Mixtures," Corrosion Science, 36, 1459-1471 (1994).

4. Oxygen Exchange

8. Åkermark, T. and Hultquist, G., "Probabilities for Oxygen Exchange in O_2 in Contact with a Solid Surface," Journal of Trace and Microprobe Techniques, 14, 377-388 (1996).

9. Åkermark, T. and Hultquist, G., "Oxygen Exchange in Oxidation of a $Fe_{70}Cr_{20}Al_{10}$-Alloy in ~10mbar O_2/H_2O-Gas Mixtures at 920°C," Oxidation of Metals, 47, 117-137 (1997).

10. Åkermark, T. and Hultquist, G., "Oxidation of Si in 15mbar Isotopically Labelled O_2/H_2O Gas Mixtures at 750-1000°C," Journal of the Electrochemical Society, 144, 1456-1462 (1997).

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Scientific Key Words: Combustion gases; Deposits; Erosion-corrosion: steels, coatings, refractories; Fireside/downstream corrosion; High temperature water corrosion; Lifetime; Steam-side corrosion

Technical Key Words: Biomass combustion; Boiler tube failures; Steam boiler; Waste-fired boiler; Pulp/paper boiler; Biomass gasification; Nuclear power systems; Corrosion probes; Steam loops

SCOPE OF RESEARCH

Fundamental Approach

'Lifetime engineering' is a theme Studsvik Material AB uses for most of the work performed. This indicates how Studsvik Material AB looks for life limiting factors and tries to assess material lifetimes in engineering applications. The high temperature corrosion research performed is mainly directed towards conventional engineering materials used at relatively low to moderate temperatures in energy conversion processes. The work is focused on environment - material interactions. Knowledge about, and understanding of, the characteristics in the environment of the energy conversion processes is essential, as well as of the material corrosion properties. The effect on corrosion from contaminants and additives in gases, deposits, steam and water is investigated.

Applications, Engineering Achievements and Technology Transfer

Energy processes such as combustion systems, gasification systems and nuclear power systems is the main area of interest. Alloys and coatings, but also ceramics and refractory materials, are dealt with. This often means steam or water cooled components and thereby moderate material temperatures, although the driving force may be the achievement of higher temperatures in a certain process for efficiency reasons.

Project customers are industry (single or multi-client), branch organizations, Swedish authorities and the European Commission.

Specific Topics

1. Biomass Co-Combustion

This is a project within Joule III in which Studsvik Material AB investigates how coal/biomass mixtures and pure biomass affect heat transfer surfaces in boilers. Corrosion mechanisms are studied so that highest possible metal temperatures may be selected in new plants. Field and laboratory experiments are performed.

2. Waste Incinerator Superheater Materials

Cooled corrosion probes and steam loops are exposed in a full scale waste incinerator, to give material selection guidelines for superheaters, to understand corrosion mechanisms and to give a path towards the use of higher steam data in new incinerator designs. The work is performed within the COST 501 collaboration.

3. Biomass Gasification

Candidate materials for raw gas coolers in biomass gasifiers are corrosion tested in simulated gas in a laboratory furnace. The materials tested are cooled to relevant metal temperatures in a hotter gas path.

4. Coatings for Erosion Protection in Fluidized Beds

The resistance to thermal cycling is evaluated for a range of erosion resistant thermally sprayed coatings. The coatings are sprayed on low alloy pressure vessel steel. Bond properties are measured before and after thermal cycling.

5. Erosion-Corrosion of Fluidized Bed Heat Exchanger Alloys

Erosion-corrosion properties of high and low alloy pressure vessel steels are evaluated by the use of an 'high temperature sand blast'. Ranking of materials are made and the transition temperatures where the erosion mode or wastage is changed, are looked for.

6. Failure Analyses of Boiler Tubes

A large number of boiler tube failure or status investigations are continuously performed for power plants and industries.

7. High Temperature Water Corrosion

Experimental studies have been carried out to verify to which extent it is possible to get passivation and oxide growth on mild steel in alkaline and salt enriched boiler water.

RECENT PUBLICATIONS

1. Open Technical Reports

1. Häggblom, E. and Nylöf, L., "Corrosion of Waste Incinerator Superheaters," Studsvik Report, M-94/40, Studsvik Material AB, Sweden (1994).

2. Häggblom, E., "Development of Superheater Materials for Waste Incinerators," Studsvik Report, M-95/190, Studsvik Material AB (1995).

3. Engman, U., "Criteria for Creation of Erosion Resistant Surface Films at High Temperatures (in Swedish)," Studsvik Report, M-95/128, Studsvik Material AB, Sweden (1995).

4. Engman, U., "Erosion Evaluation of Refractories," Thesis for the Degree of Teknologie Licentiat in Materials Science, UPTEC, 95 043R, Department of Technology, Uppsala University, Sweden (1995).

5. Falk, I., "Corrosion on Boiler Tubes," Värmeforsk, 557, The Thermal Engineering Research Institute, Sweden (1995).

6. Engman, U. and Häggblom, E., "Exposure of Cooled and Uncooled Materials in Simulated Gasification Environment," Värmeforsk, 577, The Thermal Engineering Research Institute, Sweden (1996).

2. Journal and Conference Papers

7. Källström, R., "Corrosion During Gasification of Biomass and Waste," Journal de Physique IV, 3, 787-796 (1993).

8. Häggblom, E. and Nylöf, L., "Corrosion of Waste Incinerator Superheaters," Materials for Advanced Power Engineering, Kluwer Academic Publishers, 1597-1607 (1994).

9. Tarkpea, P., Engman, U. and Olsson, M., "Laboratory Erosion-Corrosion Testing of FBC Heat Exchanger Materials - Influence of Test Parameters," Materials at High Temperatures, 13, 139-146 (1995).

10. Engman, U., "Erosion Testing of Refractories - a New Testing Procedure," Wear, 186-187, 215 -223 (1995).

11. Olsson, M., Tarkpea, P. and Engman, U., "Erosion-Corrosion Characteristics of a 2.25 Cr-1 Mo Steel Exposed at Low Particle Velocities," Tribology International, 28, 107-117 (1995).

12. Nylöf, L. and Häggblom, E., "Corrosion of Experimental Superheater Alloys in Waste Fuel Combustion," Corrosion/97, Paper No. 154.

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Scientific Key Words: Coatings; Erosion-corrosion; Sulfidation; Chloridation

Technical Key Words: Boilers; Fluidized bed combustor

SCOPE OF RESEARCH

The main activities are towards a better understanding of the performance of thermal sprayed coatings under conditions of high temperature attack, which can be corrosion, erosion or a combination of both. Corrosion types of major interest are oxidation, sulfidation and molten salt corrosion, as they are found on boiler components in coal, straw, oil and waste fired boilers.

Besides the chemical composition of the coating materials, special emphasis is put on the role of coating microstructure which is mainly influenced by the spray technique. Spray and fuse, HVOF and arc wire spraying are the techniques evaluated for this area of applications.

Specific Topics

1. Erosion of Functionally Graded Coatings Under Fluidized Bed Conditions

This project was realized in cooperation with the Corrosion and Protection Centre of UMIST. The aim was to study the potential of functionally graded coatings in a laboratory setup simulating the conditions encountered in fluidized bed boilers. The effects of particle size of the erodent and temperature as well as the amount of hard phases in the coating have been analyzed.

2. Coatings for High Temperature Corrosion Protection

This project is also partly realized as a laboratory study with the Corrosion and Protection Centre of UMIST. The aim of the project is to compare a range of coating alloys applied with different coating techniques under conditions typical for those found in boilers. Corrosion kinetics, as well as the corrosion mechanism for the different types of coatings, are analyzed to get a basis for future development of protective coatings for high temperature corrosion protection.

RECENT PUBLICATIONS

1. Heath, G.R., Stack, M.M., Rehberg, M. and Kammer, P.A., "The Erosion of Functionally Graded Coatings Under Fluidized Bed Conditions," Proc. 3rd International Conference on Structural and Functional Gradient Materials, 10-12 October 1994, Pub. EPFL, Ecublens, pp511-518 (1995).

2. Heath, G.R., Polak, R., Tsujita, T. and Gustafsson, S., "Role of Thermal Spray Coatings in Boilers; Development of Reliable Spray and Fuse Coatings for Boiler Protection," NTC '96, Cincinnati, USA, October (1995).

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4. Kretschmer, I., Heimgartner, P., Polak, R. and Kammer, P.A., "New Fusible Alloys with Enhanced Corrosion Resistance," UTSC '97, Indianapolis, Indiana, USA, September (1997).

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Scientific Key Words:	Chemical additives to water; Deposits; Erosion-corrosion; Impurities; Marine corrosion; Salt deposits; Steam; Steam-side corrosion
Technical Key Words:	Combined cycle system; Condensate (dew-point/downtime) corrosion; Emission control equipment; Steam turbine

SCOPE OF RESEARCH

Fundamental Approach

The scope of research covers topics on turbomachinery and its associated equipment related to aqueous-, steamside- and atmospheric corrosion and to deposits. The method of working is direct participation on commissioning of new, and trouble shooting at operating, power plants, as well as targeted R&D work both in the laboratory and on-site.

Applications, Engineering Achievements and Technology Transfer

Basic investigations support both the development of new, as well as the improvement of traditional, products. An important part of the practical work is performed ‘full scale’ in power plants. Direct application and technology transfer is given as the laboratory is part of the business unit responsible for power plants.

Specific Topics

1. Steam/Water Cycle Chemistry

Work is undertaken to define and optimise the chemical environment in power plant cycles, with regard to the prevention of deposits and corrosion. One important topic is the formation of brines, like hot caustic and concentrated salt solutions or of acids in steam turbines and their influence on materials behaviour. An 'Early Condensate Sampler' was developed which can be installed in the power plant to produce laboratory samples of part of the environment in the steam turbine. Results show that acidic impurities concentrate at low steam moistures, while the alkalising conditioning agent ammonia does not, resulting in a lower local pH. Other work is done to choose optimum steam/water conditioning in combined power plant cycles. Boiler water chemistry is studied by Gabrielli, F., and his group at ABB-Combustion Engineering.

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SCOPE OF RESEARCH

1. Oxidation Behavior of Five Low-Alloy Structural Steels at 600°C

Oxidation of five structural steels at 600°C in three atmospheres (air, pure oxygen and a simulated kiln atmosphere) was studied. Laboratory weight-loss test results indicated the steel designated ST2 possessed better oxidation resistance than the A36 (UNS K02600), A515 (UNS K02800), A588 (UNS K11430) and SM (designated name) steels. Thermogravimetric analyses for 24 h revealed the kinetics of oxidation for the steels studied were linear in air and in pure O_2 in the initial 0.5 h. This was followed by a transient kinetic pattern between linear and parabolic. Similar kinetics were observed for steels in the kiln atmosphere, except that linear behavior was not seen in the initial 0.5 h. Rate constants and the time exponent of the rate law for the three atmospheres could not be used to predict long-term oxidation behavior (18 days to 20 days), because each alloy possessed different spalling characteristics for its product scales in long-term oxidation.

In air oxidation, the product scales contained a porous outer Fe_2O_3 layer and a compact inner Fe_3O_4 layer. The difference in long-term weight loss resulted from a difference in the relative amounts of the inner/outer layer. For oxidation in pure O_2, the product scales on the ST2 and A588 steels were compact and adherent, whereas those on the A36, A515 and SM steels were blistered and spalled. Therefore, the former two steels suffered less long-term weight loss than the latter three. In the simulated kiln atmosphere, the product scales on the ST2 and A588 steels were composed of Fe_3O_4. Cr addition inhibited the formation of FeO, but did not segregate at the scale-metal interface. Conversely, product scales on the A36, A515 and SM steels were composed of a duplex scale of both Fe_3O_4 and a less protective FeO. Therefore, the former two steels were consistently more resistant to oxidation in the environment studied.

2. *Roles of Silicon and Aluminum in High Temperature Oxidation Behavior of Low Alloy Steel Ingots in a Simulated Combustion Atmosphere*

The effects of (0.5-2%) Si and (0 or ~0.4%) Al contents in a low alloy steel ingot on high temperature oxidation in a simulated combustion atmosphere (N_2-6.55 CO_2-18.84 H_2O-3.7 O_2) at 1050°C have been investigated. The experiment methods include thermogravimetric tests and analyses of oxidation products. The results indicate that the major oxidation kinetics obeyed a parabolic rate law, and diffusion of Fe^{2+} in the FeO layer was the rate-controlling step. Increase in Si content decreased oxidation because the FeO + Fe_2SiO_4 layer between the scale and the substrate became more compact or thicker. The effect of Al depended upon the Si content. At 0.5%Si, alloying with Al reduced the oxidation due to the segregation of $FeAl_2O_4$ at the scale/base metal interface. At 1%Si, Al promoted oxidation due to the doping effect of p-type semiconducting oxide by small amounts of Al^{3+}. At 1.5 and 2%Si, Al did not affect oxidation, because the effect of Al was inhibited by the large amount of Si.

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Scientific Key Words: Aluminides; Coating design; Intermetallics; Oxidation/Sulfidation; Refractory alloys

Technical Key Words: Waste incineration; Coal gasification; Petrochemical industry

SCOPE OF RESEARCH

Fundamental Approach

The goal of the research is to study the high-temperature corrosion behavior of Fe-base binary alloys (containing Fe-Al, Fe-Cr, and Fe-Mo), with emphasis on their corrosion mechanisms, reaction kinetics in different corrosive environments (both sulfidation and oxidation/sulfidation). This is done to establish the basic data-base for the high-temperature corrosion research and set-up more incorporated research studies with other researchers in Taiwan. In addition, effects of metallic or intermetallic coatings (namely refractory-alloys and/or refractory-aluminide intermetallics) on the protection of high-temperature corrosion have also been studied.

Applications, Engineering Achievements and Technology Transfer

With the experiences from fundamental studies, most of laboratory's work is used for practical industrial applications, such as those involved in municipal waste incineration, coal gasification, and petrochemical industry. The detailed studies of research projects are described as follows.

1. The High-Temperature Sulfidation Behavior of Grid Materials for Incinerator

This 3-year project started from 1994 is a part of the whole research of "the high-temperature corrosion of grid materials for incinerator", and has been performed in collaboration with Tsai, W.T., Professor, Hsieh, K.-C., Professor and Wang, C.J., Dr. The whole funding is supported by the National Science Council of the Republic of China. The goal of the research is to study systematically high-temperature corrosion problems of grid materials (AISI 310 SS-base alloys) for the municipal incinerator, including oxidation, sulfidation, chloridation and mixed-gases corrosion. Emphasis relating to high-temperature sulfidation is being placed on the effects of sulfur partial pressures on the sulfidation behavior of 310 SS. The sulfidation mechanism and reaction kinetics are being explored. Alloying additions (with Mo and Al), and surface coating of refractory-aluminides to enhance the sulfidation resistance of 310 SS, have also been undertaken.

2. The High-Temperature Corrosion of Fe-Al-Base Alloys in Mixed-Gases Environments

This 3-year work started in 1995 and is a part of the whole research of “development and applications of Fe-Al-base alloys”, and has been performed in collaboration with Lee, P.Y., Professor, Wu, K.J., Professor and Chu, J.P., Dr. The whole funding is also supported by National Science Council of the Republic of China. The goal of this work is to study entirely the high-temperature corrosion of Fe-Al base alloys in $H_2/H_2S/H_2O$ mixed-gas environments, having an appreciable partial pressure of sulfur and low partial pressures of oxygen. Research emphasis is being placed on high temperature corrosion of Fe-18, 29, and 40 at.% Al alloys (being α-Fe solid solution with Al, Fe_3Al and FeAl phases). Development of ternary element additions and surface treatment (coatings) to enhance corrosion resistance of the above alloys is also assessed.

RECENT PUBLICATIONS

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Scientific Key Words:	Oxidation/nitration; Titanium alloys; Diffusion; Melts; Corrosion in liquid metal environments
Technical Key Words:	Aeronautical/space propulsion system; Airframe materials; Engine materials; Surface engineering; Nuclear power systems

SCOPE OF RESEARCH

The sphere of scientific researches of the Department of High-Temperature Strength of Construction Materials in Gas and Liquid Metal Mediums (the Head of the Department is Fedirko, V., Prof.), includes:

1. High temperature interaction of the airframe materials with gaseous working and technological media.

2. High temperature interaction of the reactor materials with melts of metals.

Fundamental Approach

1. Titanium and its alloys are used widely in mechanical engineering due to a unique combination of their properties. One of the features of titanium is its high ability to interact with a gaseous medium. As a result of such interaction, a layer of chemical products (such as oxides, nitrides, oxinitrides), or a diffusional gas-saturated, near-surface zone (or simultaneously both - layer and zone) are formed on the surface of the metal. In some cases it is attempted to use titanium chemical activity (during the

chemical-thermal treatment), in others - on the contrary, to neutralize maximally (during thermal treatment and under the exploitation conditions). In this connection, the problem of thorough and complex research of physical-chemical processes (phase-formation, gas saturation, sublimation), of high-temperature interaction of titanium alloys of different structural classes and alloying systems with controlled gas media, including unstationary conditions (cyclic oxidation/nitridation) arose. The influence of such interaction consequences on the physico-mechanical properties of the metal is also investigated.

2. Environmental safety and effectiveness of nuclear reactors functioning in many respects are determined by the type of working medium, including the type of the heat-transferer. Unique thermal-physical, nuclear and radioactive properties of metal melts with low temperature melting point (Li, Pb, Na and others) makes them indispensable as a heat-transferer. Long-term work on construction materials in the liquid metal medium under the simultaneous action of high temperature and loading led to the study of corrosion processes which took place under such conditions. The researches include thorough study of structure and mechanical properties evolution of pure metals (V, Nb, Ta, Fe) and also of some heat-resistant alloys and steels during long-term contact with lithium and lead melts. The main attention is paid to the investigation of non-metal admixtures (O, N, C) and their influence in liquid metal on its corrosive aggressiveness with respect to construction material and also to the study of the conditions of oxide (carbide, nitride) layers formation regarding their protective functions, mechanism of their growth, adhesion and failure. Separate researches are devoted to the investigation of liquid metal embrittlement of different materials during deformation in melted metal.

Applications, Engineering Achievements and Technology Transfer

1. This project is aimed to establish the interrelation between the parameters of gaseous medium, as a regulating factor, and the intensity of the physico-chemical processes at the metal-environment interface, as the object of the regulation. This allows formation of the surface layers of necessary structure and phase composition and development of new technological processes of the surface strengthening for a wide range of titanium alloy products, especially in aviation (hydrohinges, hydroaccumulators of landing gears), nuclear power plants (turbine blades) and the chemical industry (base reinforcements, valve systems, pump working wheels, gearing).

2. The results obtained make it possible to choose the corrosion-resistant metallic materials which work in contact with lithium and lead heat-transfer and also to work out new and improved existing construction materials.

Specific Topics

1. High-Temperature Interaction of Titanium Alloys with Rarefield Gas Medium

The investigations are carried out together with “ANTONOV” Aircraft Scientific and Technical Complex in order to solve the problems of aircraft material sciences and technologies. The aim of these investigations is to establish the general regularities of high-temperature interaction of titanium alloys of different structural classes with inert and rarefield gas medium (vacuum, media which contain oxygen and nitrogen); to establish the principles of controlled intensity of physico-chemical processes that take place on the interphase boundaries of metal-gas system; to work out the technologies and to improve the parameters of non-oxidizing high-temperature thermal treatment while the high quality of the metal surface will be preserved.

2. Surface Engineering of Titanium Alloys in the Control Gas Medium

The purpose of the investigation is to establish the regularities and mechanisms of functional surface layer formation in titanium alloys in order to improve the operating properties (heat resistance, wear resistance, corrosion resistance and fatigue strength) of the products. The corresponding functional layers are formed due to the surface alloying of titanium alloys with the non-metal admixtures from the gaseous medium containing oxygen and nitrogen. The saturation is conducted under the isobarothermal conditions as well as under the conditions of cyclic change of gas medium parameters.

3. Corrosion of Vanadium and its Alloys in Liquid Lithium

The investigations were conducted together with the Institute of Metallurgy of the Russian Academy of Sciences (Moscow). The mutual aim of work was to predict the behavior of different vanadium alloys which contact with lithium heat-transfer in thermonuclear reactors. Corrosion tests in lithium are coordinated (approved) with planned researches of construction material properties in the frames of INTER international project. The researches are directed at the study of the influence of nitrogen and carbon non-metal admixtures dissolved in lithium upon nitride and carbidlithium on the nitride and carbide formation, exchange of admixtures between solid and liquid metals and the role of admixtures in the formation of solid metal structure.

4. High Temperature Corrosion of Armco-Iron, of Fe-Cr Model Alloys and Some Heat Resistant Steels in a Lead Melt which Guided the Controlled Content of Oxygen

The work is fulfilled in accordance with a conceptual project of a high-safety reactor on quick neutrons with passive, radiation-stable and high-boiling lead heat-transfer (the development of the project was made in the frames of former USSR). The aim of the work is to investigate fundamentally the influence of oxygen admixtures in a lead melt on the corrosion behavior of non-alloyed iron and some heat-resistant high-chromium steels and alloys. The main attention is paid to the development of a model concept about the corrosion of the mentioned materials in lead heat-transferer with different contents of oxygen admixture; determination of mechanisms of liquid metal penetration into the solid and the role of oxygen in the change of corrosion mechanism.

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Scientific Key Words:	Oxidation; Refractory metals; Refractory borides and carbides; Ceramics corrosion; Coatings
Technical Key Words:	Surface engineering

SCOPE OF RESEARCH

Fundamental Approach

The thrust of the researches, concerning high-temperature oxidation of refractory metals (Zr, Hf, Ta) and titanium binary compounds (TiC, TiB_2, TiH_2), is on the effect of purity and content of different additives on the peculiarities and mechanism of oxidation process. Because the development of wear- and corrosion-resistant ceramics with working temperatures up to 1550°C is one of the main tasks in the materials science, significant attention is paid to investigation of high-temperature corrosion properties of these ceramics (Si_3N_4, SiC) and also A1N-Si_3N_4-based composite ceramics containing metallic binder (Ni, Cr, Al). Herein, the possibility to obtain the protective nickel alumochromite barrier layer preventing further oxidation is considered.

Part of such studies is carried out in the frame of INTAS-94 Programme with the collaboration of the Institute for Problems of Materials Science, Kiev, with Limoges University (France), University of Karlsruhe (Germany), and Petten Institute of Advanced Materials (The Netherlands).

The other aspect of studies direction relates to development of laser and electroerosion coverings, with the use of titanium magnetite and datolite concentrate of boron ore, as well as spraying of laser coatings from oxynitride ceramics, electrospark coatings on hard alloys, and investigation of regularities of surface layer formation under action of concentrated solar irradiation.

Besides, the high-temperature nitriding of zirconium was studied under the conditions of solar irradiation; the mechanisms of corrosion of copper-based electrocontact materials used in low-voltage devices in chemically active media (NH_3, CO_2, H_2S, H_2S + NH_3) were defined.

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Scientific Key Words: Oxidation; Life prediction; Thermal cycling; ODS alloys; Intermetallics; Surface modification/coating

Technical Key Words: Nuclear power systems; Aerospace engine materials/coatings; Structural materials; Heat exchangers; Scale mechanical/ chemical failure

SCOPE OF RESEARCH

Since retiring from heading the High Temperature Corrosion Group at the UKAEA/AEA Technology, Harwell Laboratory in 1993 activity has been as a Materials Research Consultant for a number of Industrial Companies and Universities, in particular Cranfield University. The main focus of these research programs is the role of high temperature oxide scales in the protection of alloys and coatings in aggressive environments, with emphasis on their mechanisms of growth adhesion, protective properties and failure by both mechanical and chemical processes.

Additionally, several study visits abroad notably to Poland, Mexico and the USA, to lecture and undertake research have been undertaken with the support of the Royal Society, the British Council and the U.S. Department of Energy.

Current Main Research Programme

Specific Topics

1. *Life Extension of Alumina Forming Alloys in High Temperature Corrosion Environments (LEAFA)*

This research is being carried out by a consortium of ten European laboratories, including Cranfield University, under the direction of Nicholls, J.R., Prof., and is sponsored by the European Commission BRITE/EURAM programme. The overall aim of the work is to understand the mechanisms underlying chemical failure of alumina scales formed on a range of commercial iron-based FeCrAlRe structural alloys in a series of aggressive environments, and how these failure processes might be arrested. A further specific objective of this project will be the development of life time prediction models.

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Scientific Key Words:	Corrosion fatigue; Corrosion under mechanical strain; Life prediction; Electrochemical measurements; High temperature water corrosion
Technical Key Words:	Steam generators; Nuclear power systems; Pressure vessel alloys; Heat exchangers

SCOPE OF RESEARCH

Introduction

The research is directed towards the assessment of environment assisted cracking, EAC, in a variety of high temperature water corrosion systems with the aim of understanding the processes occurring and developing improved life prediction data. Electrochemical measurements of the properties of oxide films and on hydrogen assisted cracking are also in progress. The group is working on the susceptibility of transition weldments and diffusion bonded joints to EAC and is modelling the stress /strain distributions in tensile specimens by finite element analysis.

Most of the research is applied and is funded by industry or related bodies such as the Health and Safety Executive. The work relates to boiler tube failures, pressure vessel alloys, nuclear power systems, steam generators and energy plant. A summary of the research activities is given below.

Specific Topics

1. *Research into Primary Water Stress Corrosion Cracking (PWSCC) of Nickel-Based Alloys and Transition Welds*

This is being performed with sponsorship from the Health and Safety Executive.

2. *Measurements on the Stress Corrosion Cracking of Transition Welds and Weld Deposits in High Temperature Aqueous Solutions*

This is being conducted on behalf of HMNII, HSE.

3. *Research into the Relationship of Stress Corrosion Cracking and Microstructure of Diffusion Bonds*

This has been performed through sponsorship by the Libyan Government.

4. *Work on the Strain for Initiation of Stress Corrosion Cracking in Low Alloy Steel in BWR Water Chemistry*

This has been performed for EPRI.

5. *Research in to Stress Corrosion Cracking and Corrosion Fatigue of Pure Iron and Iron-Based Alloys in High Temperature Water*

This research is continuing and was originally funded under an EPSRC / National Power co-sponsorship.

6. *Corrosion Fatigue and Stress Corrosion Cracking of Steels in High Temperature Water and Condensing Steam*

7. *Cracking of Nickel Alloys in Hydrogen-Steam Environments*

8. *Interaction of Stress and Environment on Stress Corrosion Cracking of Stainless Steels in High Temperature Water*

9. Life-Time Predictions for Structural Components in Nuclear Power Generation Plants

The research group has collaborative links with research institutes in China and with the University of Zambia.

The laboratory is equipped with a variety of static and refreshed loop autoclaves allowing constant displacement, slow strain rate and fatigue loading. Palladium thimbles for determination of hydrogen partial pressures in-situ are also available along with the electrochemical and electron microscopy support facilities.

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SCOPE OF RESEARCH

Fundamental Approach

The activities of the High Temperature Corrosion Research Group involve:

(i) fundamental research; (ii) application-related research; (iii) technology transfer.

The fundamental research involves studies of the processes of scale formation and scale breakdown, focusing attention on species transport and scale adhesion. Such research areas relate to degradation studies in bioxidant (sulfur-and chlorine-containing media and in environments promoting hot corrosion and oxidation). The information gathered from such programmes of research is being used to design degradation resistant coatings and alloys.

Applications, Engineering Achievements and Technology Transfer

The application-related research involves the development of the processes to produce these coatings and studies of the environmental compatibility of these materials. The support and collaboration required to carry out the Group's programmes of research have come from the UK EPSRC, EU-BRITE, industries - Rolls Royce, Johnson Matthey, C-UK, British Gas, 3M and Government agencies - DTI and National Health Research.

The Research Group has developed a series of national and international networks with: Interdisciplinary Research Centre in High Performance Materials at Birmingham University; Cranfield University; University of Hull; Thessaloniki University in Greece; University of Limerick; University of Madrid and Venezuela University. The network activities not only embrace highly relevant applied and fundamental research but are also conducted to facilitate technology transfer.

Specific Topics

1. An Investigation of the Oxidation Resistance of Novel Diffusion Coatings for Turbine Components

Platinum aluminide diffusion coatings provide excellent protection for turbine components against the aggressive environments in which modern aero gas turbines operate. This EPSRC funded project, in conjunction with Rolls Royce plc, Chromalloy UK Ltd and Johnson Matthey, is concerned with the design and development of novel aluminide systems. Areas of research include the characterisation of 'new generation' platinum aluminides, the development of other noble metal aluminide systems incorporating a number of noble metals in combination and adding a series of active elements. The effectiveness of these new coatings is being assessed by comparing their high temperature degradation resistance to that of commercially available platinum aluminide coatings. The objectives are to understand the development of the protective scale, the way the scale can be retained, the creation of reservoirs of elements to sustain the formed protective scale, the rôle of inter-diffusion of the substrate/coating elements in promoting or undermining the effectiveness of the protective scales and the influence of the reactive elements on scale integrity.

2. Assessment of the Oxidation Resistance of High and Low Aluminum Activity Platinum Aluminum Coatings

High aluminum activity platinum aluminide coatings, such as RT22LT, provide protection for turbine components against oxidation and corrosion attack. This is due to the promotion of a protective alumina-based oxide scale. The integrity of the scale can, however, be undermined by either contamination or by the diffusion of damaging substrate elements. This EPSRC funded study, in conjunction with Chromalloy UK Ltd, assesses the oxidation resistance of a low aluminum activity platinum aluminide coating to determine whether, in comparison to RT22LT, the coating is less susceptible to the degradation mechanisms and so has superior performance.

3. Degradation of Ceramics and Ceramic Composites

The advanced ceramics are not only good structural materials but they are also potential high temperature (HT) degradation resistant coating materials. In this project the sulfidation and chloridation behaviour of Si_3N_4, ZrO_2 toughened alumina (ZTA) and Si_3N_4/TiC composites is being investigated at temperatures between 1100 -1400 °C. These materials showed high stability and resisted degradation in these environments. The formation of a predominantly glassy SiO_2 provides protectivity at low temperature <1100 °C but accelerated corrosion occurs at higher temperature due to N_2 evolution through the SiO_2 scale. The formation of cracks in $Zr0_2$ materials due to monoclinic tetragonal phase change at 1170 °C poses a problem while a compact adherent layer associated with the sintering additives in ZTA provides the expected protection. The work is in progress.

4. Studies of High Temperature (HT) Environmental Compatibility of Intermetallics

This project is being carried out in collaboration with the IRC in Materials for High Performance Applications at the University of Birmingham. The main aims of this project are:- to establish the HT degradation mechanisms of a number of Ti-aluminides containing Nb and Mo in high pS_2, high pCl_2, low $p0_2$ environments.

Systematic corrosion studies of a number of Ti-aluminides containing Nb and Mo alloys are being carried out in $0_2/S0_2$, $H_2/H_2S/H_20$, $H_2/HCl/H_20$ and $Ar/Cl_2/0_2$ atmosphere at 700 to 1000 °C. The derived environments include low oxygen ($p0_2=10^{-11}$-10^{-13}Pa), high sulfur ($pS_2 = 10^{-1}$-10^{4} Pa), high chlorine ($pCl_2 = 10^{-3}$-10 Pa) activities. The materials for this project are being processed by plasma melting, spray forming and spray forming + HIPing at the IRC at Birmingham University.

The main objectives are:

(i) to study the scaling kinetics; and

(ii) to establish the degradation mechanics of these intermetallics.

5. Development of Refractory Metal Coatings by Pack Cementation to Combat high Temperature Sulfidation

This project has been designed with two main objectives:

(i) to develop a pack cementation process to produce multi-element coatings using a single step (or a minimum number of steps); and (ii) to use this process to produce refractory metals and multi-element coating using appropriate powder mixtures, temperature and pressure.

The first step has been planned to obtain a better understanding of the thermodynamics and kinetics of the solid/gas reactions involved and other processes occurring in the pack, using appropriate software and hence to define the best experimental conditions to be used. The information generated will be used to deposit first the single elements Nb and Mo, followed by the co-deposition of multiple elements together with the reactive metals, preferably in a single step, on Fe-based aluminum-containing alloys. Evaluation of such coatings in high pS_2 low $p0_2$ environments of 700 to 900 ^{0}C will constitute the second phase of the project.

Attention will be focused on several issues:

1. the development of Al_2O_3 scale;
2. the formation of refractory metal sulfide scales; and
3. the incorporation, location and rôle of the reactive metals.

6. Modeling of Erosion/Corrosion using Neural Network

In the design of high temperature coatings and materials for use in gas turbines, power generation, incineration plants attention needs to be paid to the problem of high temperature erosion and corrosion. Damage due to this conjoint action of erosion and corrosion is significantly influenced by a number of variables including temperature, environment, particle velocity, angle of impingement and particle shape and size. This project is concerned with the development of a neural network capable of predicting erosion rate as a function of the main variables mentioned above.

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Scientific Key Words:	Alloy creep relaxation/cracking-spalling; Bond/thermal barrier coatings; Finite element analysis; Intermetallics: oxidation, alloying, plasma-sprayed coatings; Titanium alloys/aluminides; Chemical failure; Corrosion/oxidation of fuel cladding in nuclear reactors
Technical Key Words:	Aeroengines; Future gas turbine materials; Land-based gas turbines; Nuclear power systems; Surface engineering

SCOPE OF RESEARCH

Fundamental Approach

One important objective of the Oxidation and High-Temperature Coatings Group is to contribute to the understanding of processes affecting the mechanical stability of protective oxide layers on a range of alloy and coating substrates. The experimental approach makes use of thermobalance measurements of the critical temperature drop to initiate oxide spallation during cooling. The variation of this parameter with oxide thickness prior to cooling is a useful indicator of the mechanisms involved in the spallation process. A second approach employs finite-element models of crack growth along the oxide/metal interface when either or both of the oxide and substrate structure can deform by creep. Such computations are currently being undertaken for both alumina- and chromia-forming alloys and/or coatings. A consistent result has been that stress relaxation at the tip of an oxide/metal interfacial crack in such systems is dominated by creep in the underlying metal substrate. The spallation characteristics are related to the creep strength of the metal and also cooling rates.

A second major activity of the Group is the modification of alloys and high-temperature coatings, both chemically and structurally, to improve high-temperature corrosion properties. Of particular interest are γ-titanium aluminides and studies are conducted of the early stages of oxidation, third-element additions and the use of overlay coatings. A significant advantage in these studies is the ability to manufacture Ti-Al intermetallics in house using the IRC's plasma melting facility. Other projects in this area involve the improvement of conventional MCrAlY-type overlay or TBC bond coats. The departmental plasma-spraying facility is used in these studies.

Applications, Engineering Achievements and Technology Transfer

Most of the work described above is undertaken in close collaboration with other academic institutions and industrial partners. Formal arrangements exist with UK, French and German collaborators through a Brite-EuRam award and with UK domestic industry through an EPSRC-LINK funded programme. Further details are provided in the project outlines given below. Applications cover most high-temperature usage such as aerospace, nuclear and fossil-fuelled electricity generation and land-based gas turbines.

Specific Topics

1. Prediction of Spallation of an Alumina Layer from Overlay Coatings

This project is funded by EPSRC and is undertaken in collaboration with Rolls Royce and the National Physical Laboratory. The overall objective is to improve methods of prediction of oxide spallation from MCrAlY coatings using both experimental and numerical approaches. A key feature is understanding the role of local surface curvature on stress generation and cracking processes.

2. Improving the Failure Resistance of Alumina Scales on High-Temperature Materials

This project is funded through the Brite-EuRam initiative of the EC. It involves close collaboration with industrial partners (Inco Alloys, Krupp VDM, Kanthal, Ugine Savoie, AEA Technology) and various universities (Liverpool, Cranfield, MPI Stuttgart, Clausthal, Paris-Sud, St.Etienne). The Birmingham role is to use numerical methods to evaluate the influence of alloy creep strength on oxide spallation.

3. Oxidation of Zirconium Alloys

Oxidation of various zirconium alloys is being performed in CO_2-based environments. The work relates to the behaviour of such alloys in nuclear reactors and is funded by Magnox Electric.

4. Early Stages of Oxidation of TiAl Intermetallics

This project examines the early stages of oxidation of γ-TiAl using Auger, SEM and AFM in order to understand the initial competition between Ti- and Al-rich oxides.

5. Surface Modification of γ-TiAl by HIP Processing

This project is undertaken entirely within the IRC of the University of Birmingham under the supervision of Jacobs, M.H., Dr. Its objective is to improve high temperature corrosion properties of γ-TiAl by alloy compositional changes and by HIPping. Active collaboration occurs with the University of Northumbria.

6. Influence of an Overlay Coating on γ-TiAl Properties

This work is undertaken in collaboration with the IRC and funded by the EPSRC and Rolls Royce. The objective is to examine possible benefits of an overlay coating system on the oxidation of γ-TiAl. The study incorporates oxidation, sulfidation and mechanical properties tests.

7. The Development of SMART Overlay Coatings

The aim of this project is to develop a new generation of 'smart' MCrAlY-type overlay coatings, capable of forming the most suitable protective oxide (eg chromia at moderate temperatures, alumina at high) for the prevailing exposure conditions. The work involves close collaboration with Cranfield University and with industry. The project is funded by the Engineering and Physical Sciences Research Council (EPSRC) and the UK Dept. of Trade and Industry (DTI) under the LINK Surface Engineering scheme.

8. Self-Healing Overlay Coating (SHOC) Technology

This EPSRC-funded project involves collaboration with Cranfield University. The objective of the research is to enhance the ability of MCrAlY-type coatings to re-form a protective oxide when the initial oxide layer breaks down.

In addition to these projects at the University of Birmingham, Evans, H.E., Dr., is involved privately as a research consultant in the following:

9. *Predicting Chemical Failure of an Austenitic Steel*

Modeling of both Cr and Si depletion profiles is being undertaken after long-term oxidation of thin-sectioned samples of a chromia-forming austenitic steel. The objective of the project is to relate the onset of chemical failure, i.e. the initiation of non-healing, non-selective oxidation, to the level of solute depletion.

10. *Interfacial Crack Propagation during Compressive Failure of Thin Protective Oxide Layers*

This project is jointly funded by the UK DTI and EPRI and is undertaken at the National Physical Laboratory under the direction of Saunders, S.R.J., Dr. Extensive laboratory tests are being undertaken on both chromia- and alumina-forming alloys to measure and model oxide/metal interfacial cracking. The approach employs TGA, XRD, AE, S-decoration and in-site mechanical testing techniques.

11. *Development of a Database on Mechanical Properties of Oxide Scales*

This EPRI-funded project is coordinated by Saunders, S.R.J., Dr., and Gohil, D.D., Mr., at the National Physical Laboratory. The purpose is to collate internationally-available data on the physical and mechanical properties of protective scales and relevant substrates. This information will ultimately be available as a database.

12. *Characterization of Protective Oxide Scales and the Conditions under which they are Formed and Retained.*

This work is undertaken at the National Physical Laboratory under the direction of Osgerby, S., Dr. It is funded by the DTI and involves close industrial links. The overall objective is to develop guidelines that will enable operators to maximise the safe and efficient operation of high-temperature plant and to predict more accurately the remanent lifetime of components.

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Scientific Key Words: Burner rigs; Coal-ash corrosion; Combustion gases; Salt deposits; Waste incinerator materials; Waterwall materials; Sulfidation; chloridation

Technical Key Words: Boiler tube failures; Furnace wall corrosion; Coal-fired boilers; Waste incineration; Fuel quality effects; Operating envelope

SCOPE OF RESEARCH

Fundamental Approach

The central thrust of the research is the study of the fire-side corrosion of alloys used in the water wall section of coal-fired and waste-fired boilers. Alloys are exposed to flames and combustion gas mixtures in purpose-built corrosion rigs. Alloy temperatures and imposed, transmitted heat fluxes are in the range encountered in plant. The combustion gas mixtures can have low oxygen potentials and be doped to produce high sulfur and chlorine potentials as well as trace metals. Research is being undertaken with pulverised coal flames which may be similarly doped and have low oxygen potentials.

Practical Applications

Corrosion studies are undertaken with alloys, and under conditions, found in power plant. The results of these studies aid the understanding of the fundamental science but equally important give practical information on the corrosion behaviour of boiler materials and their operating envelopes.

Specific Topics

1. *Corrosion of Materials for Sub-Stoichiometric Combustion, Gasification and Waste Incineration. Phase III - The Role of Trace Metals.*

This work is funded by the Engineering and Physical Sciences Research Council, National Power and Powergen. The fireside corrosion of alloys used in coal and waste-fired boiler evaporator (waterwall) tubes is being studied in a purpose built rig. The alloys are exposed to flames doped with trace metals found in typical fuels. The aim is to elucidate the role of these trace metals chlorine and sulfur in the corrosion mechanism.

2. *The Role of Chlorine in the Corrosion of Carbon Steel Used in the Waterwall of U.S. Boilers.*

This work is funded by EPRI and the Illinois Clean Coal Institute. The fireside corrosion of carbon steel used in the waterwall of coal-fired plant is being studied in a purpose-built pulverised coal-fired rig. The ultimate aim is to elucidate the role of chlorine in the corrosion mechanism.

RECENT PUBLICATIONS

Until recently all the work has been undertaken in commercial confidence.

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Scientific Key Words: Hot corrosion; Ceramic fibre reaction products; Composites; Waste incinerator materials

Technical Key Words: Engine materials; Coal-fired boiler; Waste incineration; Gas turbines; Engine materials

SCOPE OF RESEARCH

This research has studied the corrosion product scales which form on Ni and Co alloys, in relation to the corrosion mechanism and kinetics. Protection and breakdown of the scales were of special interest. Applications of this research include marine gas turbine engines, coal gasifier systems and waste incinerators. Atmospheres used range from high oxygen activity with SO_2, to low oxygen activity with sulfur and chlorine.

Specific Topics

1. Oxidation and Sulfidation of Ni, Co and Fe Based Alloys

These were studied in simulated waste incinerator and gas turbine environments (SO_2 + O_2 and CO + CO_2 + H_2 + H_2S + N_2 respectively). XRD, SEM and XPS were used to investigate corrosion products. At 625° and 750°C the initial stages were simultaneous nucleation of Cr_2O_3 and NiO, CoO and FeO. Subsequent corrosion mechanisms involve thermodynamically stable sulphates reacting with cations giving a mixture of oxides and sulfides (from XPS studies). High Co and low Ni alloys have the best corrosion resistance, helped by high Cr and Si.

2. Coatings for Hot Corrosion Resistance

These have been studied, in relation to problems such as substrate compatibility, adhesion, porosity, possibility of repair/recoating, interdiffusion, effect of thermal cycling, wear and corrosion resistance

RECENT PUBLICATIONS

1. High Temperature Corrosion in Aggressive Gases

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Scientific Key Words: Chromia/alumina adhesion; Oxide growth-mechanisms; Reactive element effect; Coatings; Finite element analysis; Thermodynamic stability diagrams; Silicon carbide

Technical Key Words: Engine materials; Ceramics components; Thermal barrier coating systems

SCOPE OF RESEARCH

The research falls into two sections. In the first the aim is to study the growth mechanisms of chromia scales and to further the understanding of the reactive element effect in chromia and alumina scales. The second section consists of research on coatings.

Specific Topics

1. *The Effects, on the Oxidation Behaviour of Fe-25%Cr and Fe-25%Cr-5%Al, of Varying the Concentrations of Yttria, Alumina and Chromia in the Scales*

In order to study the effects of incorporating different amounts of yttria and alumina into the chromia scale formed on Fe-25%Cr,and of yttria and chromia in the alumina scale formed on Fe-25Cr-5Al, while keeping the composition of the alloys constant, thin oxide films containing various amounts of yttria, alumina and chromia have been deposited on the alloys prior to oxidation. An electrochemical method was used to deposit the films from organic nitrate salt solutions. The research is being carried out in co-operation with Huibin Qi, Dr. of the University of Science and Technology, Beijing, as a Royal Society Anglo/Chinese Joint Project.

2. The Growth-Mechanism of Chromia Scales Formed on Chromium

Oxygen-18 is used as a tracer and imaging SIMS is used to study its distribution in the scale. The research is being carried out in co-operation with Vickerman, J.C., Prof., of the Chemistry Department, UMIST.

3. Integrated Oxidation Protection for Carbon Fibre-SiC Matrix Composites

This research is being carried out in co-operation with Daimler-Benz Aerospace (Dornier),M.T.U.(Germany), Cerhol (Holland),Sintec-CVD(U.K.)and C.S.I.C.(Spain), and is sponsored by EEC BRITE-EURAM. The objective of the program is to develop multilayer oxidation protection systems for carbon fibre-SiC matrix composites. Thermodynamic calculations are being made using MTDATA to predict most promising systems. Finite element analysis is being performed using LUSAS to ensure that selected coatings will be mechanically stable during production and use. Coatings have been deposited by the other partners. Mechanical and thermo-mechanical tests are being carried out on coated samples. An integrated test rig has been built with a capability up to 1600°C. Tests are being performed and the mechanisms of coating breakdown studied by SEM.

4. Mechanical Properties of the Bond Coat in Thermal Barrier Coatings

The mechanical properties of MCrAlY coatings are being investigated with the aim of determining their influence on the failure of thermal barrier coatings. The role of composition and oxidation is being studied. The program is supported by Volvo Aero Corporation.

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Scientific Key Words: Life prediction; Erosion-corrosion; Hot corrosion; Burner rigs; Gasification; Multicomponent gas mixtures; Thermal cycling

Technical Key Words: Combined cycle system; Air-blown gasifier; Coal gasification; Hot gas filtration; Ceramic filter durability; Gas turbines-coal-fired; fluidised bed combustor

SCOPE OF RESEARCH

Fundamental Approach

The main aim of the research is to support the development of coal-fired, combined cycle power systems by ensuring that appropriate data are available to permit the selection of the most suitable materials for component construction throughout the systems. The behavior of a wide range of materials from heat exchanger alloys to gas turbine blading alloys and coatings to ceramic filter materials is being investigated in a number of work programs. The main thrust of this work has been to determine the potential lives of components in specific environments within coal-fired combined cycle power systems. To meet this objective, there has been an extensive exposure program of materials in British Coal's pilot plants. Wider ranges of materials have been exposed in laboratory tests specifically designed to simulate particular component environments. To determine the performance of metallic materials in all the environments being studied, a highly accurate metrology method, devised for the Grimethorpe Topping Cycle development programme, has been widely applied during

1993-97. This assessment method allows statistically valid, accurate measurements of metal loss to be made. When combined with detailed information of exposure conditions, these data allow models of materials performance to be produced for particular types of exposure conditions, eg gas turbine hot gas paths, coal gasifier hot gas paths, etc. For hot gas clean-up systems, the performance of ceramic filters has been extensively studied in both coal combustion and gasification systems.

Applications, Engineering Achievements and Technology Transfer

Most of CTDD's materials work is undertaken to support the development of clean coal-fired, combined cycle power systems. The development of these power systems is undertaken by British Coal in collaboration with a number of other companies. During the review period of this report, there have been two major development programs: the Grimethorpe Topping Cycle Project (GTCP) carried out by British Coal in collaboration with PowerGen, GEC Alsthom, UK DTI and EPRI; the current Air Blown Gasification Cycle (ABGC) development program, which is being carried out in collaboration with GEC Alsthom, Mitsui Babcock Energy, PowerGen and the UK DTI (as the UK Clean Coal Power Generation Group). In support of these major development programs, numerous distinct projects address specific aspects of these complex combined cycle power systems. These supporting projects are carried out with appropriate groupings of universities, research institutes and other industrial partners as necessary. These programs of work are underpinning the successful development of coal-fired combined cycle power systems, in terms of both materials selection for components (eg, heat exchanger for fluidised bed combustors, fuel gas coolers, coal gasifiers, hot gas clean-up units, gas turbines, etc) and process development. Whilst the results of many of these programs of work are confidential to specific project partners, papers are published in the open literature on the general topics being investigated as well as on specific methods and rigs developed for the programs.

Specific Topics

1. Materials for Gasifier Hot Gas Path Components in Advanced Combined Cycle Plants

This work is being carried out for the European Coal and Steel Community (ECSC) and the UK DTI in support of the ABGC development program. The overall aim of the project is to widen the range of applicability of earlier models of materials performance in coal gasifier hot gas paths to include the effects of deposits, welding and mixed high temperature/downtime exposures. This project is continuing to produce a large amount of materials performance data from well controlled laboratory tests for up to 4,000 hours. Tests are investigating the effects of realistic ABGC deposit compositions, welds, etc. Thermal cycling tests are investigating the spalling of corrosion products under slow and fast cycling conditions. Specialised test facilities for some of these tests have been built, eg for fast thermal cycling tests. Sets of materials have been exposed to well characterised gas streams in CTDD's coal gasification pilot plants: appropriately cooled probes have also been used in these plants to obtain realistic ABGC deposits. Wherever appropriate in the project, materials performances have been assessed using accurate dimensional metrology.

2. Effects of Contaminants on Materials Performance in Industrial Gas Turbines for Advanced Combined Cycle Power Plants

This project forms part of an ECSC programme on 'Hot Gas Cleaning' involving Kema, Rhienbraun, DMT, CRE, TPS and CSIC: CTDD's activities are sponsored by the ECSC and the UK DTI in support of the ABGC development programme. CTDD's overall aim is to define the maximum contaminant levels which will give acceptable service lives for ABGC fuel gas fired gas turbines. Deposition probes have been exposed downstream of a gas turbine combustor on a CTDD gasifier to obtain realistic deposits for an ABGC gas turbine. A series of laboratory hot corrosion tests have been carried out by CTDD and Cranfield University to investigate materials performance under specific deposition conditions. A new burner rig design (see 7 below) has been used to obtain information on ash impacting gas turbine materials at up to ~300 ms^{-1} and 1400°C. This rig is now being used for vapor deposition and corrosion tests under simulated ABGC gas turbine conditions.

3. Erosion-Corrosion of Advanced Materials for Coal-Fired Combined Cycle Power Generation

This research program, completed in 1993, was carried out in collaboration with Cranfield University, the EC Joint Research Centre at Petten, the UK National Physical Laboratory, VITO and University of Manchester Institute of Science and Technology, with sponsorship from the European Commission JOULE Programme. The program produced life-prediction models for candidate materials in selected gasification and gas turbine environments in coal fired combined-cycle power generation systems. CTDD co-ordinated the project and provided details of the environments needed for the study, as well as exposing a range of materials in coal gasification pilot plants (ductwork and heat exchanger alloys) and the Grimethorpe PFBC facility (ductwork and gas turbine materials) to well characterised gas streams.

4. Grimethorpe Topping Cycle Project (GTCP)

This project, completed in 1993, involved the investigation of candidate materials in a wide range of environments. The performance of heat exchanger materials (for evaporators and superheaters) in an optimised PFBC tube bank design was characterised to check that it met design criteria. The degradation of candidate ductwork materials was evaluated throughout the PFBC hot gas path. The behavior of a range of coated and uncoated gas turbine materials exposed on static probes, in a cascade and in a single stage gas turbine weas evaluated. A highly accurate dimensional metrology method was used to assess the metal losses of materials exposed throughout this program: the general method allows measurements to be made on components ranging in shape from simple cylinders (eg heat exchanger tubing, probes, etc) to gas turbine aerofoils.

5. *PFBC Ceramic Filters*

A program of work, sponsored by EPRI, has been under taken in collaboration with the UK National Physical Laboratory to characterise the performance of ceramic filter materials in PFBC environments, in terms of their mechanical and chemical stability. Filter elements from a number of PFBC facilities have been studied, as well as those characterised by CTDD for the GTCP.

6. *Gasifier Filter Units*

The performance of ceramic filter elements and other parts of hot gas filter units (eg springs, venturis, pulse pipes, etc) used in CTDD's gasifier pilot plants have been monitored for a number of ECSC and UK DTI sponsored programs in support of the ABGC development.

7. *CTDD Materials Burner Rig Facility*

During the course of CTDD's investigations of materials performances in coal-fired combined cycle gas turbines, it became necessary to test candidate materials as realistically as possible, in the absence of an ABGC gas turbine. To meet the required exposure conditions, a burner rig has been designed, built and has been operating since early 1996. This burner rig is gas fired and of a ducted design which allows gas streams of up to 1400°C to be accelerated up to ~350 ms^{-1}. To achieve the desired environments, the rig uses particulate, liquid and gas injection systems to add particles, vapors and gaseous species, respectively, to the combusted gas stream. The facility can be used to expose cooled or uncooled materials to the hot gas stream, and so simulate realistic deposition scenarios. The exposure conditions within the automated facility are monitored using computerised data logging and gas analysis systems.

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Scientific Key Words:	Coated superalloys; Computerized databases; Life prediction; Mixed oxidants; Oxide mechanical properties; Spallation/ cracking modeling
Technical Key Words:	Fossil fuel-fired boiler; Petrochemical industry; Gas turbines; Coal gasification; Surface engineering

SCOPE OF THE RESEARCH

Fundamental Approach

The National Physical Laboratory is the UK's standards laboratory and, as such, has the responsibility for the maintenance of fundamental standards such as mass, length and time, as well as development of new standards and test methods for a wide range of physical and material properties. Thus it is in that context that the majority of research on high temperature corrosion and coatings is set.

The main topics being pursued are inter-related and acknowledge the importance of mechanical stability of the protective oxide or coating that may be used. While scale growth kinetics, ie diffusion barrier characteristics, and thermochemistry, ie chemical stability of protective oxide scales are reasonably well understood, optimised properties for these two parameters are of little use if the system has poor mechanical stability. The same comments are, of course, equally applicable to protective coatings. These main research topics are supplemented by work on high temperature corrosion testing in a number of different environments where data for industry are needed, as well as the development of databanks and definitions of 'safe' operating regimes for various alloy systems.

Applications, Engineering Achievements and Technology Transfer

The main application areas are in the power engineering (power generation, gas turbines, aerospace and automotive) and petrochemical sectors. The main engineering achievements are seen in the effort to establish a degree of standardisation in test and measurement methods. To date progress has been slow but, with the increasing acceptance of accreditation to quality systems (ISO 9000, for example), the need for these standards is becoming more generally accepted. Considerable emphasis is placed on technology transfer by our main customer, the UK Department of Trade and Industry (DTI), and to that end various dissemination vehicles are being used. Industrial advisory groups are set up to advise on the direction of current and future work. Collaborative research projects, direct contact by visiting industrial establishments and contacts at conferences are seen as the most effect means for dissemination at a detailed level. Wider dissemination is achieved by Newsletters, mailshots, Internet pages and press releases.

CURRENT RESEARCH TOPICS

Specific Topics

1. Protective Oxides Scales, Conditions for their Formation and Retention

This work is funded by DTI, and aims to improve test methods for the determination of fracture strain (flexure and uniaxial), particularly at high temperature, oxide growth stress, scale adhesion (scratch, indentation and four-point bend tests) and the development of scale failure maps. The work on adhesion is integrated with analytical modeling of laminar composites where there is considerable potential for cross-fertilisation. In addition, test methods are being developed to determine the effects of downtime corrosion that occurs in coal gasification systems, and the definition of safe operating conditions for two alloys, mild steel and alloy 800, in respectively, combustion and coal gasification conditions as a function of sulfur- and chlorine-containing impurities.

2. Development of a Database on the Mechanical Properties of Protective Oxide Scales

Jointly funded by EPRI and DTI, this work aims to develop a computerised database for the mechanical properties of oxide scales and other relevant data, such as some important substrate properties (creep, thermal expansion coefficients, etc), that will allow the user to design components for high temperature operation in aggressive environments more effectively.

3. Interfacial Crack Propagation and Scale Fracture on Low Alloy Steels

Funded by EPRI, this research aims to develop predictive methods for scale spallation by investigation of interfacial failure associated with the wedge cracking spallation mode. Special emphasis has been placed on chromia and alumina scales. The experimental work uses sulfur decoration methods to determine the onset and extent of spallation as a function of temperature and hold times during controlled cooling cycles, and this is supported by a finite element study of the phenomena. Associated with this task is an investigation of fracture behaviour in tension and compression of oxide scales grown on low alloy steels to assist in the prediction of boiler steel behaviour.

4. Mechanical Properties of Oxidation Resistant Gas Turbine Coatings

The work aims to develop improved test methods for measurement of thermal mechanical fatigue (TMF), ductile brittle transition temperature (DBTT) and coating adhesion. The research is sponsored by DTI and is carried out in association with a European collaborative project, COST 501, which involves all the main European gas turbine engine manufacturers and coating suppliers. Adhesion test method development will pursue a similar strategy to that described in Project 1 above, while for the TMF work a novel electro-thermal rig is being used to simulate the relevant strain/temperature cycles, and for DBTT uniaxial and flexure tests are being investigated. The test methods are being studied against a background of three coating development work-packages on high strength MCrAlY, optimisation of PtAl coatings and new coatings for γTiAl.

5. Hardness and Young's Modulus Measurement Using Depth Sensing Indentation (DSI) Instruments

This work is also funded by DTI and is the NPL research input to an international project involving about 50 different organisations as part of the VAMAS (Versailles agreement on Advanced Materials And Standards) programme. NPL has management responsibility for the technical work area on mechanical properties of thin films and coatings (TWA22). Direct measurement of properties of thin films is not possible using DSI instrument in-plan because of substrate interactions, so that either analytical or numerical modeling methods are necessary to determine the coating properties. Active experimental and modelling groups are participating in the overall programme of the TWA to compare the output of experimental work with the predictions of the different models. In the first instance the research is restricted to two systems of a soft coating on a hard substrate (aluminum on sapphire) and a hard coating on a soft substrate (alumina on aluminum). Further projects within this TWA are anticipated, of which a study of adhesion is expected to be the next topic to be launched.

6. Standardisation of Test Methods for Isothermal High Temperature Oxidation and Corrosion Tests (TESTCORR)

The aim of this project is to develop a standard procedure for conducting isothermal hot corrosion tests. The work is partially funded by the European Commission with matching funds from DTI and it is managed by Electrical Research Association. Partners in the project include Cranfield University, Max Planck Institute Dusseldorf, ENEL, VDM, Swedish Metals Research Institute, Kanthal, Avesta Sheffield and Petten. The research aims to specify specimen geometry, surface preparation, furnace entry procedures, heating and cooling rates, example atmospheres that simulate specific types of industrial environments and importantly post-test evaluation procedures. NPL's specific responsibility is the examination of surface roughness effects and in defining pre- and post-test evaluation methods, as well as taking the lead in ensuring adoption of the standard by relevant committees.

7. Quantitative Measurement of Localised Strain

A major problem with most strain measuring methods is that at best the measured value is averaged over an area of a few square millimetres. Use of electron backscattered diffraction patterns (EBSP), or measurement of hardness by nanoindentation methods, gives the possibility of micron scale spatial resolution. In both cases the main challenge to achieving this objective is the development of a reliable calibration procedure. In addition, for nanoindentation an improved analytical procedure is needed, whereas for EBSP digitisation of the channelling patterns produced by the method is required in order to quantify the line broadening associated with increasing strain. The work in funded by the Defence Research Agency and has the supplementary aim of providing a method of validating FE simulation of stress distributions in components.

8. Development and Validation of Mechanical Property Measurement of Thin Coatings

The work is sponsored by the European Commission as part of the Standards Measurement and Testing (SM&T) Programme and aims to develop a suite of test methods for a number of important properties of coatings; these include measurement of thickness using acoustic microcopy, scratch adhesion testing, abrasive and sliding wear test methods and the determination of Young's modulus by indentation, acoustic microscopy and impact excitation. Fourteen main partners are involved in the UK, Germany, France, Belgium and The Netherlands. The output from this work will be a direct input into draft European standards (CEN), and an ancillary deliverable will be the production of certified reference coatings.

9. Automated Grain Size and Orientation Determination

The work is funded by the NPL from central funds, and aims to develop a fully automated method to determine grain size and orientation. While this is now possible using computer intensive methods, coupled with EBSP, a novel approach making use of forward mounted backscattered detectors will, in principle, allow acquistion of data in a matter of minutes rather than hours. The main challenge is the definition of an image analysis method to identify grain boundaries. The need for the work arises from the fact that process modelling has now reached a stage where optimised structures can be defined and process variables adjusted to allow production of such structures, but there is a lack of a suitable measurement method.

10. Test Facilities

While no specific research projects exist, test facilities are available and frequently used by industrial customers for the determination of carburisation and hot-salt corrosion resistance (burner rig testing) and creep corrosion testing in complex gas mixtures.

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Scientific Key Words: Cyclic oxidation; Erosion-corrosion; Waste incinerator materials; Chloridation; Sulfidation; Carburization; Metal dusting

Technical Key Words: Biomass combustion; Waste incineration; Stirling engines; Gas turbines; Valve alloys

SCOPE OF RESEARCH

Currently two collaborative projects are being set up, one on a life prediction test for cyclic oxidation and the other on application of TLA to high temperature erosion corrosion.

A critical literature survey on corrosion in waste incineration is also being conducted.

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Scientific Key Words:	Computer modeling; Interfaces; Point defects; Silicon oxidation; Zirconium alloy corrosion
Technical Key Words:	Engine materials; Fuel cells; Membranes; Nuclear power systems; Surface engineering

SCOPE OF RESEARCH

Fundamental Approach

The aim of the research on oxidation and corrosion in the UCL Centre for Materials Research is to understand the fundamental processes involved, and hence to develop quantitative predictive tools which will aid materials design and lifetime/reliability assessment. The work is based on computer models, which range from atomic-scale through mesoscopic (microstructures such as grain structures) to continuum treatments. In practical situations, all these levels are relevant: for example, mass transport of reacting species takes place at the atomic level, is generally more rapid along grain boundaries, and is dependent on strain. The work of the group covers the oxidation of metallic systems as well as that of silicon, with applications ranging over high-temperature alloys, nuclear reactor components, and semiconductor systems.

The Centre is also active in the modeling of bulk ceramic materials and ceramic coatings. The fundamental approach is similar to that for oxidation, with models covering a range of length scales. These models have been simplified and brought together to describe plasma and chemical deposition methods of coating information.

Applications, Engineering Achievements and Technology Transfer

Much of the Centre's work is concerned with developing computer models based on sound physical principles, which are then applied to practical problems in materials design and performance. This work is often carried out in conjunction with industrial partners, as is shown by the abstracts which follow.

Specific Topics

1. Oxidation of Silicon

This work (in conjunction with AEA Technology under a European Commission programme) aims to understand the fundamental processes involved in the oxidation of silicon. The aim of the work is to show how better control may be exercised both over the quality of the silicon-silica interface and over the uniformity of the oxide thickness. Both of these are critical issues in the manufacture of semiconductor devices.

2. Development of Models of Metal-Ceramic Interfaces

The Centre maintains and develops the atomistic modeling codes HADES, MIDAS and CHAOS (originally written at Harwell Laboratory). The current areas of activity are in the calculation of interfacial energies between metals and ceramics, and the influence on them of lattice defects. New methods of computing interatomic potentials, particularly necessary in oxide ceramics, are also being developed.

3. Dopant Effects on Zircaloy Oxidation

Calculations (in conjunction with AEA Technology) have shown the importance of the charge state of dopant species in zirconium oxide in inhibiting the nodular corrosion of Zircaloy. Dopants which differ significantly in charge from the host cations have strong effects on ion transport, and hence on the corrosion rate. The underlying idea of small concentrations of dopants having crucial effects on the nature of oxidation is of great significance to many high temperature alloys.

4. Water Chemistry and Corrosion in PWRS

Calculations (in conjunction with AEA Technology) have investigated the mechanism whereby zinc addition to the coolant in a PWR reduces the activity trapped in the oxide films. Calculations of the energetics of substituting zinc for cobalt and nickel in the spinel show that the mechanism cannot be a simple substitution reaction. A combination of calculation and examination of the experimental evidence strongly suggests that the role of zinc is to block grain boundary migration and so prevent normal film growth and the uptake of cobalt in the film.

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Scientific Key Words: Erosion-corrosion; Wear; Chloridation; Oxidation/sulfidation; Alumina; Internal oxidation; Reactive-element effect

Technical Key Words: Fluidized-bed combustor; Combined-cycle system; Gas turbines; Coal gasification; Resistance-change microsensors

SCOPE OF RESEARCH

Fundamental Approach

The thrust of 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 transport processes within such scales and has been extended to very corrosive situations where protective scales are not developed or maintained. Examples include coal-conversion and waste-incineration environments where oxygen potentials are low and sulfur or chlorine potentials are high, gas-turbine environments where molten salts may be deposited and fluidized-bed coal combustion or catalytic-cracker conditions, where impact erosion by solid particles may cause degradation. Extensive programs have also examined the role of oxides under sliding-wear conditions. In some situations, the effectiveness of metallic and ceramic coatings for protection has been studied. The High-Temperature Group in the Corrosion and Protection Centre has set up a collaborative venture with the Coatings Technology and High-Temperature Materials Group in the School of Industrial and Manufacturing Science at Cranfield University, to study thin-film sensors for monitoring mixed-gas oxidant systems at high temperature. The Group is also part of a network of ten high-temperature laboratories in Europe, funded by the Human Capital and Mobility Programme, involved in high-temperature corrosion testing of alloys.

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 as expected for a department in the top category in the recent research assessment exercise in the UK, covering work over a four year period. These include fluidized-bed combustors, combined-cycle systems, catalytic crackers, gas turbines and coal gasifiers. The work is often undertaken in conjunction with consortia of industrial partners, or single sponsors, as indicated in the following abstracts.

Specific Topics

1. High-Temperature Oxidation of Ferritic Alumina-Forming Alloys of the Iron-Chromium-Aluminum Type

This research is being undertaken in collaboration with Prunier, V., Dr. and is supported by Electricité de France. It involves a fundamental investigation of the oxidation of alumina-forming alloys based on iron-25% chromium-5% aluminum at 1100° to 1300°C. The aim is to develop a detailed understanding of the mechanisms of oxidation as a basis for optimization of alloy composition for effective long-term exposure under isothermal and thermal-cycling conditions. Emphasis is being placed on the influence of reactive elements on performance.

2. The Role of Internal Stress on the Transition from Internal to External Oxidation

High-temperature alloys usually contain sufficient chromium to ensure development of a Cr_2O_3-rich scale for oxidation resistance. This project is concerned with the transition from internal to external oxidation of chromium in nickel-chromium alloys. Emphasis is being placed on determination of the parameters that influence this transition and, particularly, the effects of internal stress generated as internal precipitates grow in a confined location on the establishment of the Cr_2O_3-rich scale.

3. *The Influence of Minor Elements on the Oxidation of Iron-Chromium-Aluminum Alloys at High-Temperature*

This research is supported by Nissan Steel. A study is being carried out into the oxidation of alumina-forming iron-base alloys at high temperatures. Emphasis is being placed on the effects of minor alloying elements, such as molybdenum, titanium, yttrium and zirconium, on the kinetics of oxidation, the mechanisms of scale growth and the resistance of the protective scale to spallation. Various electronoptical techniques, particularly analytical transmission electron microscopy, are being used to study the morphologies and compositions of the scales and to determine the locations of the minor elements after oxidation.

4. *Investigation of the Reactive Element Effect on the High-Temperature Oxidation of Alloys Using Electrochemical Techniques*

The beneficial effect of reactive-element additions, such as yttrium or cerium, on the high-temperature oxidation behavior of alloys is well established. Reactive-element additions result in improved scale integrity and a reduction in scale growth. Although there is no general consensus on why such additions are beneficial, it has been postulated that the reactive element suppresses cation diffusion. The purpose of this work is to test the validity of these ideas by carrying out electrochemical measurements on the oxidation behavior of nickel and nickel-chromium alloys, with and without reactive-element additions. Solid-state impedance studies are being used to assess the change in ion transport for such alloys.

5. *High-Temperature Thin-Film Conductance Sensors for Gaseous Sulfur-Containing Species*

This project is being undertaken in collaboration with Nicholls, J.R., Professor, of Cranfield University and is supported by the Engineering and Physical Sciences Research Council. The aim is to investigate materials for deposition as thin films for sensing, by conductance methods, sulfur-containing gaseous species in high-temperature mixed-gas systems, including oxidizing (air/SO_2) and reducing (H_2/H_2S) environments. The studies at Cranfield University are concerned with the influence of coating parameters on the structures and conductivities of the sensing materials, leading to the ability to tailor the sensor to specific applications.

6. *High-Temperature Corrosion Testing*

A network of ten European laboratories involved in high-temperature corrosion research has been set up to contribute to the development and standardization of high-temperature corrosion testing, to study corrosion under conditions of real practical interest and to encourage the exchange of experience and training of young scientists.

The main thrust of the research is to study corrosion processes in various environments at 500° to 650°C. The emphasis of the UMIST work is on the effects of chlorine on such processes, under both high oxygen- and low oxygen-containing gases. The network is funded by the European Community under the Human Capital and Mobility Programme. The collaborating laboratories are Max-Planck-Institut fur Eisenforschung (Grabke, H., Professor), Universita de Genova (Gesmundo, F., Professor), University of Delft (de Wit, J.H.W., Professor), Joint Research Centre, Petten (Norton, J.F., Dr.), Universidad Complutense de Madrid (Perez Trujillo, F.J., Professor), University of Limerick (Pomeroy, M., Dr.), Research Centre Julich (Quadakkers, W., Dr.), Institute Nationale Polytechnique de Toulouse (Pieraggi, B., Professor) and the Karl-Winnacker Institute der Dechema (Schutze, M., Dr.).

7. The Corrosion Behavior of Binary and Ternary Nickel-Base Alloys in Oxidizing/ Chloridizing Gases at High-Temperature

A study is being undertaken of the corrosion resistance of Cr_2O_3- and Al_2O_3-forming alloys in oxygen containing various concentrations of hydrogen chloride at high temperatures. Volatile corrosion products are being collected and their influence on the effectiveness of the protective oxide scales is being investigated, using various electronoptical techniques.

8. Thermal Spray Coatings for High-Temperature Corrosion Protection

The research is being undertaken in collaboration with Heimgartner, P., Dr. and is supported by the Engineering and Physical Sciences Research Council and Eutectic-Castolin. It is a study of the degradation resistance of thermal spray coatings in environments pertinent to waste-incineration processes. The exposed specimens are being evaluated in terms of reaction kinetics and compositions and morphologies of corrosion products, with emphasis on establishing mechanisms of corrosion and developing a sound technical base for design of corrosion-resistant coatings.

9. Rapid Thermal Cycling of Alloys in Coal-Gasification Environments

This research is being undertaken in collaboration with Oakey, J., Dr. and Simms, N., Dr. and is supported by the Engineering and Physical Sciences Research Council and Coal Technology Development Division. Untreated high-temperature coal-gasification environments can be very aggressive, often being sulfidizing, oxidizing or carburizing. The project is a study of the performance of iron- and iron-nickel-base alloys in such gases under conditions of rapid thermal cycling from high temperatures to 200°C. The results are being compared with those for specimens exposed under similar but isothermal conditions, in an attempt to understand the mechanisms of degradation or protection and to ascertain the important parameters for the selection of a resistant material for application in gasification plant.

10. Corrosion of Alloys by High-Temperature Molten Glass

This project is supported by British Nuclear Fuels Limited. Vitrification plant for the processing of high level nuclear waste requires materials compatible with molten glasses to temperatures of about 1050°C. The corrosion rates of high-temperature alloys in simulant molten glass are being determined to identify the most appropriate alloys. Effects of environment chemistry and stress on corrosion processes are being investigated. Consideration is also being given to possible surface treatments of the alloys.

11. Sliding Frictional Wear of Materials at Elevated Temperature

This research is supported by a Sino-British Friendship Fellowship. It is a study of the sliding friction and wear behavior of alloys in controlled gaseous environments at temperatures to 800°C. Previous research has shown that formation of oxide glazes at elevated temperatures can be beneficial in protecting the surfaces of components in sliding contact in air. This research is an investigation of the influences of other gaseous species on this phenomenon, with emphasis on the effects of water vapor on establishment of oxide glazes on nickel-base alloys. The worn specimens are being examined by various electronoptical techniques, enabling mechanisms of wear or protection to be ascertained. Models to account for the processes are being established.

12. Erosion-Corrosion of Materials Under Sulfidation Conditions Pertinent to Catalytic-Cracker Systems

This research is being undertaken in collaboration with Lotz, V., Dr. and, more recently, Donnelly, M. Dr., and Lewis, K., Dr., and is supported by Shell International Oil Products. The aim of the project is to undertake a systematic study of the synergistic interactions of erosion and corrosion under multiple impact conditions at elevated temperature in closely-controlled gaseous environments pertinent to catalytic-cracker plant. Emphasis is being placed on the influence of sulfur in low oxygen-containing gases on the modes of erosion damage of a range of high-temperature alloys. The important material and environment parameters which influence erosion-corrosion behavior are being assessed and mechanisms of degradation or protection ascertained.

13. The Influence of Temperature on the Erosion-Oxidation of Alloys

The project is supported by CONACYT. Earlier research has shown that the erosion damage of alloys increases with increase in temperature under fluidized-bed conditions, due to a detrimental effect of oxidation. However, above a critical temperature, the oxides developed can give some protection and the rate of degradation decreases with further increases in temperature. In this research, a detailed investigation of the influence of erosion variables, such as particle size, velocity and alloy composition, is being undertaken to obtain a better understanding of the transition from erosion-corrosion- to corrosion-dominated degradation behavior.

14. Modeling the Elevated-Temperature Erosion-Corrosion of Alloys and Graded Coatings

The purpose of this work is to extend existing models of erosion-corrosion to simulate erosion-corrosion of alloys and novel (graded) coatings at elevated temperatures. The models will be used to demonstrate the physical significance of the erosion-corrosion regime (through use of computer graphics) as defined on an erosion-corrosion map.

15. Elevated-Temperature Erosion of Ni-Cr/WC-Based Functionally-Graded Materials

The research is supported by COLCIENCIAS. Although there has been much work carried out on the erosion of conventional alloys at elevated temperature, there has been little work done on advanced materials, such as composites or graded coatings. In this study, the effects of particulate volume fraction, impact velocity and temperature are being evaluated for a range of bulk materials of candidate functionally-graded Ni-Cr/WC coatings. The results are being used to generate erosion maps for functionally-graded materials and MMCs at elevated temperatures.

16. Erosion-Corrosion of Coated Alloys at High Temperature

This project is being carried out in collaboration with Prunier, V., Dr. and is supported by Electricité de France. The aim is to evaluate the erosion-corrosion resistance of alloys and coatings for possible use in circulating fluidized-bed combustors. Tests are being carried out in a spouting-bed facility and a jet-impingement facility, enabling a wide range of erosion variables to be obtained. Thickness-change measurements correlated with talysurf profiling, morphological examinations and analyses of the surfaces are providing valuable information on the effectiveness of coatings in protecting surfaces under such conditions.

17. The Development of a Mathematical Model for Erosion-Oxidation of Alloys in Low-Velocity Conditions

This research is supported by the Engineering and Physical Sciences Research Council. The objective is to develop a fundamental model of the synergistic interactions of erosion and oxidation for alloys in low-velocity conditions at elevated temperatures. The work involves modeling the effects of erosion variables, such as impact energy and particle concentrations, and oxidation variables, such as properties of the environment and temperature. A further aim of the work is to establish the effect of variation in oxide growth laws on the erosion-corrosion rate. The model is being used to establish a theoretical method for construction of boundaries on erosion-corrosion maps. These maps are potentially useful in identifying the combination of parameters which change the erosion process from erosion of the alloy substrate to erosion of the oxide layer.

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Scientific Key Words: Sulfur segregation; Chromia/alumina adhesion; Reactive element effect; Auger electron spectroscopy; Scanning transmission electron microscopy; Ceramics/molten aluminium; Composite interface reactions

Technical Key Words: Heating elements; Surface engineering; Catalyst support systems; Engine applications

SCOPE OF RESEARCH

Fundamental Approach

The main theme throughout the work at Liverpool is the use of high spatial microanalytical techniques to study the segregation of minor elements and impurities such as sulfur and carbon during the development of oxide scales on a wide variety of metals and alloys. This work covers the whole range of reactions from the earliest stages of oxidation at the submonolayer level on high purity, single crystal metals, right through to the chemical failure of scales on complex alloys, which become susceptible to breakaway attack after prolonged periods of oxidation at high temperatures. A combination of electron microscopy with EDX and PEELS analysis, surface analysis using Auger and XPS techniques, and scanning tunneling microscopy is being used in all these cases.

Applications, Engineering Achievements and Technology Transfer

Most of the work is of a fundamental nature, but related to practical materials and situations, as might be expected for a department which was placed in the top category in the recent research assessment exercise in the UK, covering work over the last four years. Specific projects are listed below.

Specific Topics

1. How to Improve the Failure Resistance of Alumina Scales on High Temperature Materials

This work is being undertaken in collaboration with groups at the Technische Universität Clausthal and the Max-Planck-Gesellschaft in Stuttgart, Germany, Université de Paris-Sud and Ecole des Mines in St. Etienne, France and Cranfield University, UK, sponsored by the European Commission under the Brite-Euram programme. The main industrial and technical objectives are the modeling of the alumina scale failure on a range of Fe-Cr-Al alloys and the specification of criteria for the improved failure resistance of alumina-forming materials. Work at Liverpool has been primarily concerned with studies of segregation of impurities to the metal-oxide interface and oxide grain boundaries during the early stages of oxidation and the composition of oxides after prolonged exposure to high temperature conditions.

2. Segregation of Sulfur to Grain Boundaries and Surfaces in Nickel Based Alloys

This work, supported by EPSRC via the Interdisciplinary Research Centre in Surface Science at Liverpool is concerned with the interplay between sulfur, carbon and oxygen on nickel surfaces. Sulfur tends to passivate nickel surfaces prior to oxidation, while carbon and sulphur compete for sites on the surface at intermediate temperatures (350°-500°C). This can have important effects on the lifetime of nickel components used in chemical plant at these temperatures, where segregation can dramatically affect performance, and further implications of this work are now being investigated in conjunction with Imperial Chemical Industries.

3. Impurity Segregation During the Early Stages of Alumina and Chromia Scale Growth

This work, supported by EPSRC, has considered the development of transient scales on alumina- and chromia-forming alloys and the effect of impurity segregation on the final structure of the scale. It has used high spatial resolution techniques, including HREM and STEM, and electron-transparent cross-sections of the metal/oxide interface, to determine the role of minor alloy additions and impurities on scale development.

4. The Oxidation of Molten Aluminum During the Squeeze Casting of Metal-Matrix Composites

This work is sponsored by The University of Liverpool and Vernaware Ltd. The oxidation of the surface of molten aluminium during the manufacture of Al/Al_2O_3 metal-matrix composites greatly affects the integrity of the castings produced. This research has considered how these oxide films affect the bonding of the metal to the fibres and the formation of casting defects at the interface between the reinforced and unreinforced regions of the casting.

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Scientific Key Words: Cyclic oxidation; Hot corrosion; Erosion; Sulfur segregation; Refractory alloys; Silicide coatings; Thermodynamic modeling

Technical Key Words: Engine materials; Future gas turbine materials

SCOPE OF RESEARCH

Fundamental Approach

The broad range of research and development activities at United Technologies Research Center includes work focused on understanding and enhancing the durability of high-temperature alloys and coatings for use in gas turbines. Investigation of the effect of impurity segregation (such as sulfur) on the cyclic oxidation resistance of aluminide coatings, overlay coatings and single crystal alloys has been the focus of several internal research programs and Navy contracts. Hot corrosion of turbine materials in the presence of molten sulfate salts is also an active area of research. Detailed investigation of erosion behavior is enabled by a unique high-temperature erosion test facility. Insight provided by these investigations has guided the development of materials and coatings with enhanced erosion / oxidation resistance. Other areas of interest include the development of future gas turbine materials (e.g., ceramic matrix composites, refractory metal-based alloys and silicide coatings) with excellent environmental resistance.

Applications, Engineering Achievements and Technology Transfer

Laboratory work involves an integrated set of fundamental and applied research programs to support the application and development of materials and coatings for service at elevated temperatures in erosive and/or oxidizing environments. Programs focus on development of materials systems for rotor, compressor, combustor, turbine, and seal applications.

Specific Topics

1. Oxidation and Hot Corrosion Resistance of High-Temperature Materials

Oxidation and hot corrosion related research has focused on identifying the effects of various segregating impurity elements on the environmental resistance of alumina forming coatings (overlay and aluminides) and single crystal alloys. Such effects are ascertained through establishing correlations between cyclic oxidation resistance, bulk elemental concentrations and surface segregation behavior at elevated temperatures. This approach has been applied to assess the impact of various impurities on oxide scale adherence and has led to identification strategies to improve the environmental resistance of alumina-forming alloys and coatings at elevated temperatures. Recent hot corrosion research has involved investigation of sulfate salt deposition mechanisms in industrial gas turbines operating in a marine environment and the durability of thermal barrier coatings (TBCs).

2. Erosion Resistance of Materials for Gas Turbines and Rotating Hardware

The focus of erosion research involves benchmarking the performance of new materials and investigating degradation mechanisms affecting the durability of materials in aero- and land-based gas turbine engines and systems used for leading edge protection of rotating structures. Material systems under study include (1) gas path sealing systems composed of elastomers, porous metals, and porous ceramics; (2) hard leading edge candidates such as engineered ceramics; (3) polymer matrix composites (PMCs) and erosion protection candidates for PMCs; and (4) conventional aluminum, titanium, and nickel-based alloys used throughout the gas turbine engine. Effects of environmental exposure (time and temperature) on the performance of materials (i.e., sintering effects) are studied to enhance understanding system behavior during extended service. Facilities are described separately below.

3. Modeling of Multi-Component Phase Equilibria for Environmental Protection

Thermodynamic modeling of condensed phases and chemical interactions between condensed and vapor species is being used to describe materials processes and predict material interactions with the environment during service. The computer program Thermo-Calc and the thermodynamic databases necessary to calculate multi-component phase equilibria in oxides, alloys and molten salts are available to perform these assessments. The databases include thermodynamic descriptions of more than

4000 compounds and gas species and about 250 alloys and solutions. By combining the thermodynamic database with a kinetic database, phase transformations controlled by diffusion can be simulated using the computer program DICTRA.

4. Advanced Oxidation Resistant Refractory Metal-Based Alloys and Coatings.

This work involves determination of phase equilibria in the alloy system of interest, measurement and modeling of the oxidation behavior, and assessment of alloy/coating diffusional stability. A recently completed program deals with the development of $MoSi_2$-based composite coatings to protect niobium-based alloys. In this case, oxidation kinetics, thermal / mechanical / chemical stability of the alloy / coating system, coatings process development, and performance evaluations were investigated.

5. Particulate Erosion Test Facility

The UTRC particulate erosion facility is housed in a 1000ft^2 laboratory. It is designed to vary independently and systematically study important particulate erosion parameters: temperatures from below ambient to greater than 1260°C, gas velocities up to Mach number 0.85, particles from 1-3000 microns in diameter, and at incidence angles from 0 to 90°. The system is comprised of nine subsections: (1) room temperature sonic nozzle air control, measurement, and delivery system; (2) set point controlled (room temperature to 540°C) electrically heated air supply; (3) set point controlled (540°C to more than 1260°C) burner heated air supply, (4) mixing chamber; (5) particle feed system; (6) 1.5 m long by 3.8 cm diameter SiC acceleration tube; (7) sample chamber; (8) diagnostics (including remote video to record the erosion process, two color optical pyrometry [370 to 1650°C], and a 4 watt argon ion laser based Laser Doppler Velocimetry, LDV, unit); and (9) a PC based computer data acquisition system for data logging. Generally, the specimen test size is 2.5 by 2 cm surface geometry but a wide variety of sizes are acceptable, including actual parts such as turbine blades and vanes.

6. Air-Cooled Thermal Gradient Burner Rig Facility

An atmospheric pressure burner rig facility capable of combusting a variety of fuels is available for testing hollow cylindrical specimens. Coated or uncoated samples are mounted in a rotating carousel downstream from the nozzle, and internal cooling of hollow cylindrical specimens is accomplished by forced air impingement. The cooling air supply is measured and controlled through the use of sonic nozzles. Inside sample wall temperatures are monitored with thermocouples supported by a slip ring assembly, and the outer surface temperature is measured with both a single color optical pyrometer at a wavelength of 8 microns and a two color optical pyrometer at a wavelength of 0.9 microns. The use of internal cooling enables testing of thermal barrier coated alloys under conditions simulating those encountered during service (i.e, the ceramic coating is exposed to temperatures exceeding the melting point of the underlying alloy/bond coating) and provides insight into factors limiting the durability of TBCs.

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Technical Key Words:	Gas turbines (aeroengines, land-based gas turbines, expander turbines); Engine materials (directionally-solidified alloys, single crystal alloys, conventionally-cast alloys, thermal barrier coating systems); Rotors; Engine applications

SCOPE OF RESEARCH

Specific Topics

1. Examination of Service Run Hardware

Field run gas turbine blades and vanes are being examined to determine the condition of the material, including the coatings. The objective of this research is to learn the operative degradation mechanisms, what influences these mechanisms, and how to reduce this degradation in the future. The focus of the effort is often upon the surface condition of the coatings and the alloys (both internal and external surfaces) since this is frequently the controlling degradation location. Repair methods and repairability of the components are also of great interest. This work is supported by various commercial companies.

2. Life Analysis/Prediction of Engine Components Including Coatings

The life of field run hardware, including the life of high temperature coatings, is being determined from analytical analysis coupled with metallurgical analysis. The objective of the work is to determine the remaining life and to extend this life. This work is supported by various commercial companies.

3. Thermal Barrier Coatings

The use of thermal barrier coatings to extend the life of gas turbine hardware is being investigated for various commercial companies.

4. Stresses in Oxide Scales

The generation of stresses in growing oxide scales, the effect of these stresses upon the substrate and the failure of these scales is being studied. This work is currently being funded internally.

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Technical Key Words:	Engine materials; Single crystal alloys; Thermal barrier coating systems; Navy engine materials

SCOPE OF RESEARCH

Fundamental Approach

The research is directed at applied problems, with emphasis on fundamental understanding. The approaches involve exposure of materials to defined conditions followed by detailed characterization using optical metallography, scanning electron microscopy and transmission electron microscopy.

Applications, Engineering Achievements and Technology Transfer

In the following the results and achievement of the current projects are briefly summarized.

Specific Topics

1. Oxidation of Intermetallics

There is currently renewed interest in intermetallic compounds as potential high temperature structural materials. However, despite the fact that many contain significant amounts of Al or Si, most intermetallic compounds oxidize at rates which are prohibitively rapid. Analysis of this problem indicates that the only structurally-useful compounds which can form oxide films which will *possibly* be protective are TiAl, the aluminides of Ni (and Fe), and $MoSi_2$. Therefore, work in this project has been focused on the oxidation behavior of TiAl, NiAl, and $MoSi_2$ and, in particular, their behavior in the temperature range 500 to 900°C. The effect of surface preparation, atmosphere composition, and alloying with Cr on the oxidation behaviour of γ-TiAl have been explained. Also, the mechanisms of accelerated oxidation of NiAl and $MoSi_2$ have been further clarified.

2. Superalloys and Coatings

High temperature alloys, depending on the application, must withstand conditions of isothermal and cyclic oxidation, corrosion by impurities in the exposure environment, and particle erosion. In cases where the alloys are insufficiently resistant to the exposure conditions they must be coated. This project is focused on the resistance of Ni-base superalloys and high temperature Fe-base alloys to this type of degradation and the use of coatings for protection. The effects of sulfur content and reactive element additions on the adherence of alumina scales to single crystal Ni-base superalloys and ferritic Fe-Cr-Al alloys are being clarified. The conditions for depositing Cr-modified aluminide coatings on Ni-base superalloys by a one-step pack cementation are being defined. It is anticipated that these coatings will have improved hot corrosion resistance compared to conventional aluminide coating. Finally, the behavior of hard nitride coatings (TiN, CrN) in exposures which combine oxidation and particle erosion is being studied.

3. Water Vapor Effects on the Spalling of Alumina Scales

A large amount of data is available in the literature on the effects of water vapor on the oxidation of metals and alloys. Examples exist where water vapor improves oxidation resistance or causes adverse effects. In the current investigation the influence of water vapor on the oxidation of alloys that develop protective alumina scales is being examined. It has been found that in the case of alloys where some cracking of the alumina occurs in dry oxidizing gases, water vapor substantially increases the amount of cracking and spalling. In cases where the alumina scales are very adherent and do not crack in dry oxidizing gas, the water vapor does not have any effect.

4. Oxidation of Titanium Matrix Composites

The oxidation of titanium matrix composites reinforced with SiC has been investigated at temperatures between 500° to 900°C in air oxygen and water vapor. The titanium matrix phase had a composition of Ti-22Al-23Nb(at%). The scales that developed on this alloy contained TiO_2 and $NbAlO_4$. The protectiveness of these scales was not adequate for extended use of this alloy above 600°C. The effects of nitrogen in air and water vapor on the oxidation of this alloy are under investigation. The SiC reinforcing phase was rapidly oxidized due to a carbon layer adjacent to the matrix phase and the carbon core used to fabricate the SCS SiC fibers.

5. Wear and Oxidation of Diamond Film

The wear and oxidation of diamond films are being studied to determine if wear may involve oxidation. Oxidation of diamond films occurs at temperatures of 500°C. It is oxygen pressure dependent increasing with oxygen pressure. Wear of diamond coating cutting tools has been determined to occur by fracturing of diamond facets in the case of machining of nonferrous materials such as Al-Si alloys. In the case of ferrous material wear of diamond occurs rapidly and involves reaction with the ferrous substrates. In neither case does oxidation of the diamond appear to be important.

6. Erosion-Corrosion of Alloys

The combined erosion-oxidation of nickel, cobalt, iron and nickel-chromium alloys is being investigated from room temperature to about 800°C. It has been found that the erosion enhanced oxidation regime can be described in terms of oxide removal for each individual erosive particle impact. When the time between particle impacts is so small that metal is removed as well as the oxide formed between impacts, the erosion rate increases at least by an order of magnitude. The cause of this increased erosion is to be investigated.

In the case of the erosion oxidation of nickel-chromium alloys, the erosion process maintains Ni-20Cr and Ni-30Cr alloys in a state of erosion-maintained transient oxidation and the chromium in these alloys has no influence on their erosion-oxidation behavior.

7. The Removal of Sulfur from Liquid Metal

There is much interest in reducing the sulfur concentrations of superalloys in order to form protective alumina scales on these alloys during oxidation. The best time in superalloy production for removal of sulfur is in the processing of the liquid alloy when there is rapid material transport and rapid reaction. Sulfur removal from liquid alloys is being investigated by using reactions with CaO and with Y_2O_3 to form sulfides and oxysulfides.

8. Durability of New Alloys for Advanced Heat Exchangers

It will be necessary to operate electricity generating plant at higher levels of efficiency in order to reduce costs and to reduce the output of greenhouse gases. This will require an increase in operating temperature to levels beyond the reach of ferrous alloys. Consequently superalloys and other advanced compositions must be selected for this application. The current project will measure corrosion and creep strain simultaneously on specimens of these materials, in order to obtain data relevant to their long-term behavior in the products of coal combustion at high temperatures.

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Technical Key Words: Coal-fired boilers; Boiler tube failures; Advanced steam conditions

SCOPE OF RESEARCH

Approach

This research is directed at coal-ash corrosion, a damage mechanism that has plagued the coal-fired boiler industry for half a century. The coal-ash corrosion research started in the mid-1970s with an extensive laboratory investigation of the variables affecting the coal-ash corrosion mechanism. These included temperature, alkali sulfate concentrations in the ash, sulfur dioxide concentration in the flue gas, and elemental constituents in the alloys and coatings. The testing was first performed in the laboratory but was later moved to in situ testing in the actual operating conditions of full-scale, commercial coal-fired boilers. Air-cooled corrosion probes were inserted in the superheater or reheater sections of three coal-fired stations. Samples of ten alloys were exposed for 4000, 12,000, and 16,000 hours. Destructive analysis was performed to evaluate the wall loss and corrosion penetration into the metal. Chemical analysis of the coals being fired and the corrosion products was also performed. All of these data are being collected in order to develop the model to predict the corrosion rate for different candidate alloys at various operating conditions (temperature, alkali, and sulfur levels).

Applications, Engineering Achievements and Technology Transfer

This work is funded by a number of sponsors.

Electric Power Research Institute (EPRI) has funded the earlier laboratory and field experiments. In the laboratory Kihara, S., Dr., of Ishikajima-Harima Heavy Industries Co., Ltd., performed over 216,000 hours of testing in the coal-ash corrosion environment. A variety of temperatures, alkali, and SO_2 levels was used to expose commercially available metals, coatings, and weld metals. That laboratory program was used to select a reduced number of alloys for in situ testing on an air-cooled retractable corrosion probe assembly. In this field, in situ testing by Foster Wheeler Development Corporation exposed 10 alloys to 16,000 hours of testing at three different coal-fired boiler stations.

Oak Ridge National Laboratory has funded the recent laboratory and field testing of both commercial and developmental alloys. The laboratory and field experimental setup were essentially the same as the EPRI program described above, with the exception that FWDC performed all the work and that the air-cooled retractable corrosion probes contained two different temperature zones for each alloy. The 16,000 hours of exposure is completed, and preliminary results are being obtained for a May 1997 meeting.

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Scientific Key Words: Coated and uncoated superalloys; Bond/thermal barrier coatings; Aluminide coatings; Platinum aluminide coatings; Overlay coatings; Spallation/cracking modeling; Life prediction; Diffusion barrier for gas turbine blades

Technical Key Words: Land-based gas turbines; Aeroengines; Thermal barrier coating systems; Conventionally-cast alloys; Directionally-solidified alloys; Single crystal alloys; Nuclear power systems

SCOPE OF RESEARCH

Fundamental Approach

The primary focus of this research program is on the oxidation behavior of coated and uncoated conventionally-cast, directionally-solidified, and single crystal nickel-base superalloys that are used in land-based gas turbines and aeroengines. A combined experimental/analytical modeling approach is implemented in order to apply the results ultimately to engineering situations. Oxidation/ corrosion data are generated in both an automated thermal cycling facility, as well as a specially designed system to evaluate the influence of contaminants in steam cooling environments. Lifetime models have been developed for aluminide, platinum aluminide, and overlay coatings, as well as for APS and EB-PVD thermal barrier coatings. Some of the individual projects have been conducted under the aegis of the joint EPRI/Southwest Research Institute Materials Center for Combustion Turbines (MCCT).

Applications, Engineering Achievements and Technology Transfer

The COATLIFE model, which predicts life for aluminide, platinum aluminide, and overlay coatings in peaking, intermediate or base-load service, is being integrated into a remaining life code (REMLIF) for General Electric Frame 6 and 7 turbines. The life model developed for thermal barrier coatings is being adopted by a gas turbine manufacturer in their design assessments for an advanced turbine system.

Specific Topics

1. Life Prediction of Bucket and Nozzle Coatings in Gas Turbines

The development of the code, COATLIFE, is being undertaken by the MCCT. This code accounts for spallation of alumina from the surface of coatings during thermal cycling (turbine shutdown), as well as for loss of aluminum by diffusion from the coating to the superalloy substrate. Calibration of the model has been achieved by using weight gain/loss data generated in an automated thermal cycling facility, and the model has recently been successfully benchmarked against field experience in one turbine design. Experimental data are now being obtained on aluminide, platinum aluminide, MCrAlY, and duplex coatings at various temperatures. Benchmarking against field experience is planned for several turbine designs.

2. Prediction of Damage and Failure in Thermal Barrier Coatings (TBCs)

A life model has been developed for TBCs that not only accounts for oxidation of the bond coat but also for sintering of the ceramic, interfacial surface roughness, bond coat creep, and geometrical curvature. Benchmarking of the model against burner rig and engine data is underway.

3. Advanced Coating Developments for Gas Turbine Components

The loss of aluminum from a coating to the substrate by diffusion represents a significant long-term degradation mode for hot section components. In order to suppress the loss of aluminum, EPRI is sponsoring a project to develop a diffusion barrier between the coating and superalloy substrate. This interlayer is sputtered on to the superalloy surface prior to coating. Preliminary results have shown a significant benefit for an MCrAlY coating on GTD-111.

4. Development of an Automated Thermal Cycling Facility

The MCCT has built an automated thermal cycling facility that can test up to 20 coated/uncoated specimens simultaneously. The hot and cold cycle times are controllable, and compressed air exiting through manifolds can cool the specimens from temperatures around 1100°C to room temperature in a few seconds. The cooling rate can be controlled to simulate the gradual shutdown of a turbine or the more rapid cooling associated with a trip.

5. Effect of Steam Cooling on Corrosion and Deposition

The objective of this program is to determine the effects of steam contaminants on hot corrosion and deposition in the cooling hole passages of gas turbine blade, vane and transition materials at temperatures, pressures and flow rates that simulate operating conditions. A closed-loop system has been constructed that circulates superheated steam at temperatures up to 1,100°F and pressures up to 30 atmospheres. The system has also been designed such that steam temperature and pressure can be independently controlled in each of the 12 specimens. Metal temperatures of up to 1600°F can also be individually controlled.

6. Boric Acid Corrosion Evaluation (BACE) Corrosion Testing Program

This program is part of the EPRI Nuclear Maintenance Applications Center's overall program to provide information regarding boric acid-induced corrosion in electric power generating plants. The objective of this portion of the overall program is to conduct tests on carbon and low-alloy steels, stainless steels, and other selected materials under prototypical power plant conditions to provide data needed to understand and control boric acid-induced corrosion in power plant equipment. Completion of the planned work will provide information that will enable utility engineers to estimate corrosion rates of components affected by leakage of borated primary water, and to define maintenance, inspection, or other procedures necessary to insure that corrosion resulting from leakage of borated primary water does not constitute a hazard to the integrity of the system.

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Scientific Key Words: Alumina; Thermal barrier coatings; Ceramics; Composites; Stress

Technical Key Words: Thermal barrier coating systems; Ceramic components

SCOPE OF RESEARCH

Fundamental Approach

The objective of our research is to establish mechanism-based quantitative and predictive relationships between the development of stresses in oxide scales and their eventual failure. This is part of the broader research interests of the principal investigator in the processing, properties and microstructures of ceramics, metal/ceramic interfaces, and fracture. The principal research techniques being used are piezospectroscopy and fracture mechanics' tests. Piezospectroscopy is a non-contact method of probing strains that is especially suited to alumina scales and has recently been used to measure the stresses non-destructively in the thermally grown oxide beneath thermal barrier coatings. The ability to measure the stresses in alumina scales and the fracture resistance of scale/alloy interfaces provides the opportunity to address both unresolved scientific issues in oxidation, such as the reactive element effect, as well as technological problems in industry.

Applications, Engineering Achievements and Technology Transfer

Much of our work is in collaboration with others both in industry and in academe, and a number of a number of the techniques developed are in transfer to companies.

Specific Topics

1. Evolution of Stress in Alumina Scales

A detailed study of the evolution of stresses in alumina scales formed on Fe-Cr-Al(Y), NiAl and various superalloys is underway. In all the scales examined the stresses are independent of oxidation time, except at early times where transient aluminas may still be present. The growth stresses vary from alloy to alloy, as well as on geometric factors, but are typically in the range of 600-1300 MPa at 1000-1200°C. One direct consequence of the independence of stress on oxidation time is that local spalling is a result of local variations in scale/alloy interfacial fracture resistance. The origin of such variations has yet to be established but is presumed to be related to impurity segregation.

2. Oxidation Induced Stresses in TBC Systems

Photostimulated Cr^{3+} luminescence has been shown to be capable of penetrating through zirconia TBCs and enables the non-destructive measurement of the stresses in the thermally grown aluminum oxide (TGO) phase to be monitored with oxidation. The stresses depend on not only the bond coat composition and temperature but also the bond-coat roughness. Damage in the TGO can be monitored by the broadening of the luminescence signal and is being evaluated as an indicator of life.

3. Phase Transformations in Alumina Films

The observation of transient alumina during the early stages of oxidation of several alloys, and the extensive variation in proportion of alpha-alumina in the scales formed on the same alloy under nominally identical processing conditions, has motivated a systematic study of the effect of dopants on the kinetics of phase transformations in alumina. In contrast to previous studies on powders, we are measuring the kinetics using time resolved reflectometry of transforming films on sapphire substrates.

4. Microstructural Development of ZrO_2 TBCs

An electron beam evaporator system at UCSB is being used to study the morphological and crystallographic features of TBCs. In contrast to other studies, we are investigating growth on alumina and placing particular emphasis on grain growth selection processes leading to the columnar microstructure necessary for strain compliant TBCs.

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Scientific Key Words: Mixed oxidants with water vapor; Phase stability diagrams; Sulfidation; Fused salts; High temperature water corrosion

Technical Key Words: Boiler tube failures; Pulp/paper boiler; Steam generators; Catalytic cracking; Surface engineering

SCOPE OF RESEARCH

The scope of work is applications specific, but an attempt is made to provide a basic understanding of the phenomena that control the processes. Sulfidation and oxidation kinetics of carbon steel have been determined in a variety of intermediate temperature regimes designed to simulate fireside conditions on the waterwalls of kraft recovery boilers. Tests have been designed to account for changing conditions, i.e., oxidizing and sulfidizing cyclic conditions. Moreover, the presence of frozen salts also plays a major role in the local environmental chemistry, and has also been investigated as it relates to its impact on the gas phase. Electrochemistry in molten salts has been used to explain the rapid corrosion of stainless steel clad tubes at air injection ports in boilers. Recent work has also focused on participating in a DOE program to develop a sensor to detect fireside corrosion in recovery boilers. In the hot water corrosion segment, oxide films of prescribed thicknesses on valve have been grown on hardfacing alloys under simulated BWR conditions and subsequently determined friction parameters with varying normal loads under sliding conditions in the actual high temperature and high pressure environment.

Specific Topics

1. Fireside Corrosion of Alloys in Kraft Recovery Boilers

Given that certain zones of a boiler can be subjected to alternating oxidizing and reducing conditions, cyclic sulfidation and oxidation tests have been completed to characterize the acceleration of the corrosion rates of carbon steel at intermediate temperatures compared with constantly oxidizing or constantly reducing conditions. Galvanic electrochemical experiments have also been completed in molten NaOH-based salts to determine the relative contribution of galvanic currents to the very rapid corrosion of 18-8 stainless steel compared with nominal passivity of carbon steel. Oxide solubility models have also been applied to this molten salt problem to elucidate composite tube failure mechanisms.

2. Selection of Alloys and Coatings for FCC Turboexpanders

Turboexpanders on fluid catalytic cracking units (FCC) operate under either partial or complete combustion conditions. The relatively high sulfur partial pressures developed under partial combustion leads to shorter lives of blade alloys compared with cases where complete combustion occurs. The combustion conditions, temperature, and operating stresses all combine to provide corrosion kinetics which are unacceptably high for typical blade alloys. Various coatings and alloys are being evaluated in an effort to extend the life of current alloys.

3. Development of a Corrosivity Sensor for Kraft Recovery Boilers

The US Department of Energy (DOE) and the American Forest and Paper Association are sponsoring a program designed to evaluate various sensor technologies that may help operators of kraft recovery boilers avoid waterwall corrosion. Current practice is to evaluate wall thickness loss at shutdowns, but the extent of loss can only be averaged over the inspection period, which is normally a few months. At present, operators do not know what specific operating variables might have caused most of the wastage. If, on the other hand, operators had some indication of real-time corrosion rates, correlations with operating practice could reduce the chance for smelt-water explosions in service. The program is managed by the Institute of Paper Science and Technology, with participation from the Pulp and Paper Institute of Canada and Battelle. The program is in its early stages, but several technologies are being evaluated currently for subsequent detailed laboratory tests, and ultimately field tests in operating boilers.

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Scientific Key Words:	Bulk oxide properties; Ceramics; Composites; Diffusion; Interdiffusion; Magnetite; Thermodynamics; Mobility in oxides; Oxide bulk and surface defects; Thermodynamics/ defects of oxide solid solutions; Zirconia ceramics
Technical Key Words:	Solid oxide fuel cells; Electrochemical microsensors

SCOPE OF RESEARCH

Fundamental Approach

The focus of the research is in the area of high temperature physical chemistry regarding thermodynamic and kinetic topics. One important area is the systematic investigation of the relationships between point defects and point defect-related properties in transition metal-containing ionic crystals and the kinetics of solid state reactions in related model systems. Another area of interest is high-temperature reactions that have potential to be used for the in-situ fabrication of metal-ceramic microstructures, including composites.

Applications

The results obtained from the fundamental research outlined above have no direct and immediate technological application. However, the understanding obtained from this research with regard to the relationships between defects, defect-related transport of matter and charge and their role in solid state reactions is of fundamental interest for many solid reactions involved in high temperature corrosion processes.

Specific Topics

1. Defects and Transport in Mixed Oxides

The focus of this program is on the experimental investigation of the deviation from stoichiometry, δ, and the cation diffusion in quasi-binary, and quasi-ternary spinel solid solutions. The spinels investigated so far are $(Fe,Mn)_{3-\delta}O_4$, $(Fe,Co)_{3-\delta}O_4$, $(Fe,Co,Mn)_{3-\delta}O_4$, $(Co,Mn)_{3-\delta}O_4$, $(Fe,Ti)_{3-\delta}O_4$, $(Fe,Cr)_{3-\delta}O_4$, and $(Fe,Ni)_{3-\delta}O_4$. Other oxide solutions studied are $(Fe,Mn)_{1-\Delta}O$ and $(Fe,Co)_{1-\Delta}O$. It was found that the majority defects in all spinels listed above are cation vacancies at high oxygen activity and cation interstitials at low oxygen activities. All cation tracer diffusion coefficients measured at high temperatures in these spinels show a minimum as a function of the oxygen activity. Cation diffusion via vacancies prevails at high oxygen activities while cation diffusion assisted by interstitials is predominant at low oxygen activities. Correlation effects in the cation diffusion in spinel solid solutions were investigated by Monte Carlo simulations. Recently, the question of the influence of the charge state on the mobility of an ion has been experimentally addressed. In two different structures it was found that the charge state of a diffusing ion changes its diffusivity, however, differently in different structures. Also, recently, it has been experimentally verified that in certain oxides the grain size influences the variation of the oxygen content with the oxygen activity. (Sponsor: U.S. Department of Energy).

2. Kinetics of Spinel Formation Reactions

The kinetics of the solid state reactions between NiO and Fe_2O_3 and between CoO and Fe_2O_3 have been studied at high temperature as a function of the oxygen activity. It was found that the kinetics follow in both cases a parabolic rate law, i.e., that they are diffusion-controlled. In both cases the parabolic rate constants decrease with increasing oxygen activity, suggesting that cation interstitials play a major role in the oxidation process. Furthermore, the experimental results suggest that the oxygen activity locally varies in the reaction zone. (Sponsor: National Science Foundation through the Cornell Materials Science Center).

3. Point Defects in Olivine

The variation of the oxygen content of fayalite, Fe_2SiO_4, and of olivines, $(Fe,Mg)_2SiO_4$, with different Fe/Mg-ratios was experimentally investigated by thermogravimetry. The results suggest that cation vacancies and holes are the most important point defects in these oxides. In fayalite, electrons are also important defects. Single crystals of fayalite and of olivines with different compositions were grown. In fayalite the iron tracer diffusion and the electrical conductivity were studied as a function of the crystal orientation and found to be anisotropic. A detailed defect modelling was performed. (Sponsor: National Science Foundation through the Cornell Materials Science Center).

4. *In-Situ Formation of Metal-Ceramic Composites, Internal Reduction of Shaped Particles and Intercalation of Layered Silicates*

(jointly with Sass, S.L., Prof. and Giannelis, E.P., Prof.)

The effort of the Dieckmann group in this project focused on partial reduction reactions, leading to metal-ceramic microstructures. The influence of processing parameters such as temperature, composition of the starting material and of the oxygen partial pressure on the microstructures obtained by the partial reduction of $(Fe,Mn)_{1-\Delta}O$ was experimentally investigated as well as the influence of different dopants. It was found that certain dopants can significantly alter the microstructures obtained, i.e., doping can be used for tailoring metal-ceramic microstructures. Recently, the influence of the way that dopants are introduced into the starting material on the final microstructure was investigated for CaO-doped $(Fe,Mn)_{1-\Delta}O$ and it was found that the way of the dopant introduction makes a difference. For the case of the partial reduction of $NiAl_2O_4$ it was investigated whether grain growth during the high temperature treatment involved in the partial reduction can be reduced by the in situ formation of a second oxide phase; it was shown that this can be achieved. (Sponsor: U.S. Office of Naval Research).

5. *Design and In-Situ Processing of Metal-Ceramic and Ceramic-Ceramic Microstructures, Including Composites*

(jointly with eight other professors)

The effort of the Dieckmann group within this program has focused on (i) displacement reactions between NiO and aluminum (and aluminum-rich alloys) and (ii) on partial reduction reactions in the Ni-Al-O system. The growth of periodic layers consisting of alumina and the intermetallic phase Ni_2Al_3 was the surprising result obtained from the displacement reactions. The partial reduction reactions focused on single crystals and bi-crystals, some doped with ZrO_2 to better understand the mechanism of the partial reduction. (Sponsor: U.S. Air Force Office for Scientific Research).

SPECIAL EXPERIMENTAL CAPABILITIES

For the experimental investigation of the variation of the oxygen content of oxides as a function of the oxygen partial pressure at constant temperature a special, non-commercial thermobalance is available which has a resolution of the order of 1 μg in flowing gases at a total pressure of the order of 0.5 atm and at temperatures up to 1400°C. A radioactive tracer laboratory is available for studying the diffusion of cations in oxides. All furnaces used for thermogravimetry, tracer diffusion, electrical conductivity and reaction experiments are controlled atmosphere furnaces, which are equipped with electrochemical cells for monitoring the oxygen partial pressure. Furthermore, an image furnace is available for the growth of ceramic single crystals for the research efforts outlined. By using the floating zone technique, single crystals of congruently melting, non-transparent materials with melting temperatures up to 2800°C can be grown.

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SCOPE OF RESEARCH

Specific Topics

1. *Corrosion and Hydriding Performance of Zircaloy 2 and Zircaloy 4 Cladding Materials in PWRs*

The corrosion and hydriding performance of Zircaloy-2 and Zircaloy-4 (with different tin and silicon contents and different fabrication routes) are discussed. Data are included from three pressurized water reactors (PWRs) to rod average burnups in excess of 50 MWd/kgU and in several different autoclave environments (360°C water, 365°C water, 365°C water with additions of LiOH, and 400°C steam). A comparison of the in-reactor and ex-reactor corrosion data shows that the most time-efficient test environment is 365°C water with LiOH additions. Post irradiation examination data show that the hydrogen pickup fraction decreases with increasing oxide thickness for all types of Zircaloy. It appears that silicon additions to Zircaloy-2 reduces hydrogen pickup by eliminating the negative effect of nickel. Both Zircaloy-2P (1.3 w/o Sn, $\geq$ 70 ppm Si, Zircaloy-2) and low-tin (1.3 w/o Sn) Zircaloy-4 are judged to be advantageous cladding alloys for high burnup PWR applications. At a rod average burnup of 50 MWd/kgU in a high temperature PWR, low-tin Zircaloy-4 shows on average approximately 60% lower oxide thickness than high-tin (1.5 w/o Sn) Zircaloy-4. Zircaloy-2P tested simultaneously with low-tin Zircaloy-4 promises even further improvement based on data at around 28 MWd/kgU. Two mechanisms are proposed to explain a corrosion rate enhancement observed at high burnups for high-tin Zircaloy-4.

2. Corrosion Behavior of Zircaloy-4 Cladding with Varying Tin Content in High-Temperature Pressurized Water Reactors

Fuel rods clad with Zircaloy-4 with varying tin content (1.33 to 1.58% SN) and annealing parameters (1.0 to 4.1 x 10^{-17} h with Q/R = 40,000°K) were irradiated in demonstration fuel assemblies in a high-temperature pressurized water reactor (PWR) to burnups in excess of 35 giga watt days per metric ton or uranium (GWd/MTU). The same cladding variants were subjected to long-term static water autoclave tests at 633°K of duration greater than 1100 days. Production fuel rods fabricated with low-tin (1.33 Sn) and high-tin (1.55 Sn) Zircaloy-4 cladding were also irradiated in regular fuel assemblies in two high-temperature PWRs to burnups up to 48 GwD/MTU. Poolside cladding oxide thickness measurements were conducted on 167 high-tin rods and 67 low-tin rods during refueling outages. The measured, circumferentially averaged, peak cladding oxide thickness values ranged from 3 to 113 μm. At high burnups, the oxide thickness on low-tin cladding was 30 to 40% lower than that on high-tin cladding. The long-term autoclave results also showed the beneficial effect of lower tin level on the corrosion rate, although to a lower degree than in PWRs. The 633 K water autoclave test appears to rank the corrosion resistance of the investigated Zircaloy-4 variants in the same order as in PWRs. Hydrogen analysis results indicate that tin level does not influence the hydrogen uptake of autoclave-tested samples. The observed in-PWR influence of tin level on the Zircaloy-4 cladding corrosion rate was incorporated in the ESCORE clad corrosion model by adjusting the pre-exponential term in the post-transition corrosion rate equation.

A corrosion rate acceleration at high burnups may be related to either hydride precipitation at the metal oxide interface or to degradation of the oxide thermal conductivity. The observed effect of tin on the uniform corrosion resistance of Zircaloy-4 in high temperature water is consistent with the corrosion mechanism that assumes the migration of 0^{2-} anion vacancies through the oxygen deficient zirconia to be the rate-controlling process. It is postulated that lower tin level in Zircaloy-4 decreases the vacancy concentration in the oxide and thereby, increases the corrosion resistance. It may be possible to improve further the corrosion resistance of low-tin Zircaloy-4 by optimizing the nitrogen and tin concentrations in Zircaloy.

3. Effects of Hydride Precipitate Localization and Neutron Fluence on the Ductility of Irradiated Zircaloy-4

The ductility of high irradiated Zircaloy-4 material was evaluated by conducting tube burst, tube tensile, and ring tensile tests on fuel cladding and guide tubes irradiated in two PWRs. The specimen fluence ranged between 9 and 12.3 x 10^{21} n/cm^2 (E > 1 MeV), and test temperatures ranged from 313 to 673 K. The average thickness of the waterside oxide layer on the specimen ranged from 12 to 114 μm. Specimens with an oxide thickness greater than about 100 μm contained regions of spalling oxide and local areas of oxide significantly thicker than the specimen average. The corresponding average hydrogen contents ranged from 40 to 674 ppm for specimens without spalling oxide and estimated to be greater than 950 ppm with spalling. Non-uniform hydride distributions were observed in the specimens due to temperature gradients during operation.

The residual ductility for these high-fluence specimens is on the order of 1% uniform plastic strain for all the specimens except for two specimens with average concentration of hydrogen greater than 700 ppm and spalled oxide. The reduction in the material ductility due to radiation damage appears to be synergistically affected by localized hydride distributions and the orientation of hydride precipitates relative to the loading direction. The extent of ductility reduction due to hydride precipitates appears to be the most for the burst tests among the three tests investigated. The tensile specimens showed different fracture modes depending on deformation temperature, hydrogen concentration, local hydride volume fraction, and hydride orientation.

Neckdown and spiral fractures were observed. Examination of fracture surfaces indicated ductile failure in the metallic ligaments separating the hydride precipitates that appeared to have failed in a brittle fashion. The ductility data are analyzed by treating the material as a composite of relatively ductile metal phase separated by more brittle hydride platelets. Localization of hydride phase with a reduced presence of metallic ligaments in the composite results in reduction of ductility. A local hydride volume fraction greater than a critical value is needed to initiate and propagate fracture across the specimen cross section thereby to reduce the ductility below a set value. A model is proposed to suggest a possible ductility minima at intermediate fluences and the effect of hydride precipitates on ductility.

4. Performance of Standard and Advanced Fuel Rod Cladding for High Burnup Application in PWRs

In- and ex-reactor corrosion behavior of a number of cladding alloys developed by ABB to meet the need for fuel rod cladding with improved corrosion resistance are presented. The cladding materials include: 1) composition and processing-optimized Zircaloy-4 (OPTIN™) and Zircaloy-2 (Zircaloy-2P), and 2) a number of alternative zirconium-based alloys outside the composition range for Zircaloys. Data on fuel rods irradiated in six pressurized water reactors to rod average burnups nearing 60 MWd/kgU and from tests conducted in two autoclave environments (360°C pure and lithiated water) are presented. In-reactor fuel rod growth and diametral creep measurements made on selected alloys are also included.

OPTIN™ cladding irradiated to rod average burnups approaching 60 MWd/kgU in a high coolant inlet temperature plant showed over 50% reduction in oxide thickness compared to high-tin Zircaloy-4 that was commonly used until the late 1980s. These data indicate that OPTIN cladding is capable of providing acceptable performance in high-temperature PWRs to fuel rod burnups beyond 60 MWd/kgU. OPTIN is the current standard cladding used by ABB for fabricating all US PWR reload fuel and for ABB Systems 80 reactors in South Korea. The high burnup capability of OPTIN cladding has been used to extend peak fuel rod burnup to 60 MWdkgU. Alternative zirconium-based alloys have been used in two alternate cladding geometries, i.e. through-wall and duplex cladding. These alloys irradiated to about 40 MWd/kgU showed approximately an additional 40% less oxide thickness compared to OPTIN. Significantly lower acceleration of corrosion rate with increasing burnup observed for these alloys compared with the alloys within the Zircaloy family attests to the potential of these alloys to support significant extension of the current-industry limit for peak fuel rod burnup of 60 to 62 MWd/kgU.

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SCOPE OF RESEARCH

The beneficial aspects of corrosion are explored and corrosion processes are used in manufacturing of new materials, surface modification and corrosion protection. Examples of such processes are:

- Hydrothermal synthesis of carbon coatings.
- Hydrothermal synthesis of diamond.
- Synthesis of carbon coatings by halogenation of carbides.
- In-situ oxidation protection of silicon-based ceramics.

Other aspects of research:

- High-temperature corrosion of non-oxide ceramics.
- Formation of carbon upon corrosion of carbides.
- High-temperature stress corrosion of ceramics.
- Hydrothermal corrosion.
- Use of Raman spectroscopy in corrosion research.

Specific Topics

1. High-Temperature Corrosion and Protection of Engineering Ceramics

Kinetics and mechanisms of oxidation of silicon nitride and aluminum nitride ceramics have been studied. Aluminum nitride ceramics retain a high level of mechanical properties at temperatures above 1000°C and possess good oxidation resistance due to the formation of protective alumina-based scales. Although silicon-based ceramics dominate high-temperature engineering applications, new composites based on AlN can challenge the leading position of Si_3N_4 and SiC ceramics. Two major groups of AlN-based materials that can be considered for structural applications at high-temperatures are:

i. AlN-SiC solid solutions and multiphase composites that can form mullite scales with better protective properties compared to SiO_2, particularly in combustion atmospheres.

ii. AlN-boride (TiB_2, ZrB_2 and other) composites that form self/healing oxide scales containing refractory aluminum borates. These compositions can be used as bulk ceramics or protective coatings for C/C composites or other materials with low oxidation resistance.

<u>Collaborators</u>: Desmaison, J. and Desmaison-Brut, M., University of Limoges, France; Porz, F., University of Karlsruhe, Germany; Lavrenko, V.A., Prof., Institute of Materials Science, Ukraine; Baxter, D. and Fordham, R., Joint Research Center Petten, The Netherlands.

2. Reliable and Cost-Effective Ceramic Components for High-Temperature Fast-Firing Porcelain Furnaces and Gas Turbines by Microstructural Control of Oxide Scales on SiC and Si_3N_4

The main objective of the project is to gain fundamental control of the microstructure and growth mechanisms of oxide scales on silicon carbide and silicon nitride ceramics. Predictive tools for scale growth and component life time prediction have been developed by mathematical modeling of complex kinetics. There is a direct feed-back to the material designers, with ceramics developed. with an improved oxidation resistance at temperatures ~1500°C, and to end-users who optimize the working regimes of ceramic parts. Protection of ceramics by in-situ formed oxide scales can lead to a major breakthrough of silicon-based ceramics in high-temperature applications.

This goal will be achieved by a unique combination of advanced characterization techniques, such as high-resolution and analytical transmission electron microscopy and micro-Raman analysis, combined with scanning microscopy, X-ray diffraction, thermogravimetry and other methods. The combination of these characterization methods, including advanced techniques for sample preparation, will allow the information on the oxide scales microstructure on the meso- and nanoscopic levels to be related to that of the material and to the exact processing conditions.

Collaborators: Nickel, K.G., University of Tübingen, Germany; Backhaus-Ricoult, M., CNRS, France; Galanov, B.A., Institute of Materials Science, Ukraine.

3. *Synthesis of Carbon Coatings on the Surface of Carbides by Etching in Halogen-Containing Media*

The purpose of this project is to explore new experimental methods for the synthesis of carbon coatings with the controlled sp^2/sp^3 ratio on the surface of carbides. This will be accomplished by the extraction of metals from the carbides by halogens and their compounds. Thermodynamic computations will be done to determine the conditions favoring carbon formation. The structure and properties of carbon obtained on the surface of carbides will be studied.

The proposed research will help to formulate the basic principles, which will allow production of carbon materials with controlled sp^2/sp^3 ratios ranging from pure graphite to pure diamond and MeC-based multiphase materials. Potential applications envisaged will be for catalysis, electronics, wear resistant and tool materials, and ceramic matrix composites. The basic science that is developed in the project may have technological applications in industry within a few years.

Collaborator: McNallan, M.J., University of Illinois at Chicago, Dept. Civil and Materials Engineering.

4. *Hydrothermal Synthesis of Carbon Films on the Surface of Carbides*

The purposes of the proposed research are the following:

- To study the interaction between selected carbides (SiC, TiC and WC) and high-temperature, high-pressure water.
- To develop a hydrothermal method for synthesis of carbon coatings with the controlled structure.

This goal of the research is to formulate the basic principles, which will allow production of carbon materials with a controlled sp^2/sp^3 ratio ranging from graphite to diamond. Potential applications envisaged will be for ceramic matrix composites, wear resistant and tool materials; however, electronic and other applications may also be considered.

United States of America

Collaborator: Nickel, K.G., University of Tübingen, Germany.

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Technical Key Words:	Aeronautical/space propulsion systems; Engine materials; Ceramic components; Combustors; Single crystal alloys; Diesel engines

SCOPE OF RESEARCH

Fundamental Approach

The emphasis of the work performed by the Environmental Durability Branch at NASA Lewis Research Center is placed on understanding material behavior in high temperature, aggressive environments. Both fundamental and applied interdisciplinary research approaches are pursued to identify the degradation mode(s) underway and to develop strategies to enhance and predict the time and temperature capability of the advanced materials for potential commercial application(s). The laboratory has an extensive effort in the study of the oxidation and corrosion of metals (typically Ni-base superalloys), intermetallics (such as NiAl and TiAl), ceramics (particularly silicon-base materials), high temperature polymeric materials, and reinforced composites of these materials. Inert and oxidative kinetic behavior of materials is studied, and durability and life under high temperature, high velocity and thermal cycling conditions are conducted. Some of the studies are evolving toward longer-term durability testing and evaluation. Computational and experimental studies are performed to elucidate the high temperature material interactions with the environment and with adjoining materials. Other studies focus on the development and performance of interface coatings in composite materials, as well as protective overlay coatings for variety of material substrates through the use of plasma spray, CVD and PVD coating deposition techniques. Thermal barrier coatings are of particular interest. Efforts are underway to understand the factors which contribute to coating failure and to acquire the data needed to improve life prediction capability. In addition, the scientists work toward the development of improved TBC compositions and architectures, as well as the use of TBCs on nonmetallic and intermetallic substrates. The individual abstracts highlight the key technical areas of interest and provide an indication of the breadth of the group's expertise.

Applications, Engineering Achievements and Technology Transfer

The primary technology development interests are in materials to be used in the hot section structural components of aerospace propulsion systems. The aerospace community is anxious to achieve greater turbine engine operating efficiency achievable through the use of lower weight, higher temperature, stable, yet cost effective, advanced materials for future propulsion systems. However, the work also provides the basic material behavior data which support other high temperature material application needs, such as are found in turbine engines for land-based power generation, automotive and diesel engines, heating elements in industrial furnaces, etc. Work is conducted closely with industries and universities through contractual and grant arrangements. There is also great interest in collaborative research with industry, academia and other U.S. governmental agencies (Space Act Agreements) where each of the technical goals can be advanced through joint research and complimentary studies.

Specific Topics

1. Alumina Scale Adhesion and Low Sulfur Superalloys

The sulfur impurity content of alumina forming NiAl, NiCrAl, FeCrAl, and superalloys is being examined as the key factor controlling scale adhesion. Isothermal and cyclic oxidation of desulfurized and sulfur- doped alloys are examined. The behavior is related to the segregation potential. A fundamental criterion for adhesion is sought in terms of available monolayers of sulfur and the thermodynamics of segregation. Hydrogen annealing continues to be used as a useful tool in producing tailored low sulfur contents in nickel-base alloys for characterizing scale adhesion versus sulfur content. Desulfurization is examined as a diffusion controlled phenomenon. The fundamental thermodynamics of segregation and yttrium-sulfur interactions are evaluated by EMP analysis of sulfides and high temperature XPS of doped and undoped NiAl, NiCrAl, and single crystal superalloys. An adhesion criterion is developed from the commercially available low sulfur, single crystal, superalloys oxidation data to specify the impurity limits that allow optimum performance of actual airfoil materials. Special alloys containing both low yttrium and low sulfur were produced to define the optimum performance obtainable with minimum processing expenditure and difficulty. Hydrogen annealing has been performed for collaborative mechanistic work with GE Aircraft Engines, the University of Pittsburgh, Max Planck Institute (Stuttgart), and the Lawrence Berkeley Laboratory. Industry patents have been awarded for desulfurization by hydrogen annealing and submitted for melt fluxing. Future research will involve:

1. Chemical quantum studies to determine sulfur effects on interface strengths.
2. Surface segregation studies to define the framework and guidelines for interface measurements.
3. Evaluation of TBC coated single crystal superalloy performance as a function of sulfur content.

   (Contact: Smialek, J.A., e.mail: James.L.Smialek@lerc.nasa.gov)

2. *Personal Computer Data Base for Cyclic Oxidation Test Data Run at NASA Lewis*

Over 25 years of high temperature cyclic oxidation data generated by testing at NASA-Lewis is being assembled as a P.C. data base. Specific weight change versus time data for a given alloy sample test can be accessed by alloy, alloy type or base, test temperature, test time, or cycle time. The alloys tested included both experimental and commercial high temperature Fe-, Co- and Ni-Base alloys such as superalloys, turbine alloys, heater alloys, coating alloys, stainless steels and intermetallics. Upon completion, the data base will be made available. (Contact: Barrett, C.A., e.mail: MSBAR@popserve.lerc.nasa.gov)

3. *Long-Term Cyclic Oxidation of Superalloys and MMC's*

The aim of this work is to evaluate the long-term cyclic oxidation behavior of MA956 superalloy and sapphire fiber/MA956 composite system at temperatures higher than those of current applications. An oxidative life model has been developed based on oxidation data, which can serve as a useful tool for engine design. Finite element analysis proved highly useful in providing an understanding of the cyclic oxidation cracking and spallation behavior of the MA956 matrix material and the sapphire fiber/MA956 composite system, by accurately predicting the direction and location of oxide cracking in both material systems. (Contact: Lee, K.N., e.mail: Kang.N.Lee@lerc.nasa.gov)

4. Thermodynamics of Aluminide Alloys

Fundamental thermodynamic measurements of constituent activities in Fe-Al, Ti-Al and Ni-Al are being taken alloys with particular emphasis on correlation of thermodynamic properties with oxidation properties. The Knudsen cell technique is used in conjunction with a high temperature mass spectrometer. This technique is based on direct measurements of activities from the vapor pressure. Due to the similarity in vapor pressure, measurements on the Fe-Al system have been done with the 'ion current ratio technique'. In this case the use of ion current ratios and the Gibbs-Duhem equation allows accurate activity measurements to be taken without any calibrating standards. The other alloys require calibrating standards. A system has been developed which allows in-situ switching between two cells, permitting the use of an internal standard. Such a system compensates for instrument variations from run to run. Measurements on the standard also provide regular checks on temperature accuracy and instrument linearity. Measurements have been taken on the entire composition range for Fe-Al at 1573 K and show very good agreement with those of previous investigators. Current work is focused on Ti-Al and Ni-Al, as well as Ti-Al-X and Ni-Al-X. The large jump in Al and Ni activity across the b-NiAl phase field has been demonstrated. The change in activity across the g-TiAl phase field is substantially smaller. Third element additions such as Cr and Nb have small effects on the activity of Al. Current work is focused on determining whether these small changes of Al activity changes induced in g-TiAl by additions of Cr and Nb play a significant role in determining oxidation behavior. (Contact: Jacobson, N.S., e.mail: Nathan.S.Jacobson@lerc.nasa.gov)

5. Oxidative Life Prediction of High-Temperature Alloys and Coatings

The thrust of this work has been to predict the time for which a protective Al_2O_3 scale continues to reform and grow during cyclic oxidation. This work has involved modeling the oxide spallation process as well as modeling Al transport within the alloy or coating to the oxide/metal interface. Modeling the transport within the alloy has been accomplished through the use of finite-difference computer codes. Most of the recent efforts have been aimed at predicting the oxidative life of NiAl intermetallics. (Contact: Nesbitt, J.A., e.mail: James.A.Nesbitt@lerc.nasa.gov)

6. Hot Corrosion Testing of NiAl Alloys and Ni-Based Superalloys

The thrust of this work was to evaluate the hot corrosion resistance of various NiAl and Ni-base superalloys in conjunction with various engine manufacturers. The hot corrosion behavior was examined in Mach 0.3 burner rigs with sea salt injections into the burner. (Contact: Nesbitt, J.A., e.mail: James.A.Nesbitt@lerc.nasa.gov)

7. Oxidation Mechanisms of Multi-Phase Gamma-Based Ti-Al-X (X = Cr, Nb, Fe) Alloys and Coating Alloy Development

The role of ternary alloying additions in improving the oxidation resistance of gamma-based titanium aluminides is under investigation. Emphasis is placed on a determination of phase/oxidation relationships by studying the oxidation behavior of single-phase and two-phase alloys selected from the same tie-line. In addition to standard oxidation experiments (eg. TGA), extensive use is made of alloy/alumina diffusion couples to evaluate alumina compatibility and oxygen permeability. In addition, the alloy Ti-51Al-12Cr at.% (patent pending) has been developed as an oxidation-resistant coating alloy for gamma titanium aluminides. The composition was selected so that the microstructure consists of the gamma phase, and a minor volume of the oxidation-resistant $Ti(Cr,Al)_2$ Laves phase. By basing the coating alloy on the gamma phase, mechanical properties and substrate compatibility are optimized. The volume fraction of the Laves phase is kept to a minimum because it is extremely brittle. Evaluation of the fatigue behavior of Ti-51Al-12Cr coated Ti-48Al-2Cr-2Nb at elevated temperatures in air is in progress. (Contact: Brady, M.P., e.mail: Michael.P.Brady@lerc.nasa.gov)

8. Environmental Durability of Ti-Based Alloys

The objective of the research is to examine the environmental behavior of titanium-based alloys for aircraft gas turbine applications. The extent of environmental degradation and the degradation mechanisms are being examined as functions of composition, temperature, time and environment. Protective coatings that address the specific degradation mechanisms and compositions of the targeted Ti-based alloys are under development. The materials of interest are those being developed for high temperature structural applications in the oxidizing environments of aircraft gas turbine engines. The studies to date have concentrated on Ti_3Al+Nb (α_2) based alloys, Ti_2AlNb (orthorhombic phase) based alloys and TiAl (gamma) based alloys. Emphasis has been placed on oxidation and interstitial embrittlement as the two degradation mechanisms of general interest. The action of these mechanisms has been quantified through the use of TGA, cyclic oxidation, hardness profiling methods (to examine for interstitial hardening that characterizes embrittlement) and through fatigue of coated and uncoated specimens. (Contact: Brindley, W.J., e.mail: William.J.Brindley@lerc.nasa.gov)

9. Cyclic Oxidation of Intermetallic Composites

The thrust of this work was to examine the cyclic oxidation behavior of continuous fiber, NiAl/Al_2O_3 and FeCrAlY/Al_2O_3 composites and make comparisons with the bulk matrix material. The extent of oxidation down the fiber/matrix interface was of particular interest as well as the effect of the fiber/matrix CTE mismatch on the oxide spalling behavior of the composite. (Contact: Nesbitt, J.A., e.mail: James.A.Nesbitt@lerc.nasa.gov)

10. Degradation Studies of High Temperature Polymeric Materials

The goal of this work is to characterize the molecular level curing, and thermal and oxidative degradation mechanisms of high temperature polymers and preceramic materials. These materials are used as matrices for composites for advanced engine applications. The ultimate objective of this work is to apply the understanding of degradation pathways to the design of improved matrix materials for these applications. High temperature and preceramic polymers are typically insoluble, intractable materials, making molecular structure characterization difficult. The approach used is to employ solid CP-MAS NMR (^{13}C, ^{29}Si, etc.) of both labeled and natural abundance samples, in combination with metallographic and other analytical techniques to study these materials. In this way, changes in polymer structure can be directly related to macroscopic, physical signs of ageing. (Contact: Meador, M.A.B., e.mail: maryann.meador@lerc.nasa.gov)

11. Thermal Barrier Coatings

An ongoing study of bond coat properties and how they influence TBC life is being conducted. The goals are both understanding of the effect of bond coat properties on the life of a TBC as well as developments that address the known effects of bond coat properties on TBC life. The study approach includes an experimental examination of the range of life attainable from different bond coat compositions, as well as characterization of the properties expected to be pertinent to TBC life. The properties found to date that correlate best with TBC life include bond coat oxidation response, bond coat creep behavior and bond coat coefficient of thermal expansion. Recent results have indicated that a variation in Y-content for an MCrAlY bond coat can have a substantial impact both on the oxidation behavior of the bond coat and the life of the ceramic insulating layer. (Contact: Brindley, W.J., e.mail: William.J.Brindley@lerc.nasa.gov)

12. Influence of Thermal Barrier Coating Microstructure on Thermal Conductivity

The influence of thermal barrier coating microstructure on thermal conductivity is being investigated. Experimental observations backed by finite element modeling have shown that the high-aspect ratio cracks in the microstructure are far more effective in blocking the flow of heat than are the low-aspect ratio pores. The thermal conductivity resulting from a complex assemblage of pores and cracks, representative of real microstructures, is being modeled under contract to Tufts University using analytical techniques that had previously been used to model the effect of microstructure of modulus. Also, NASA is working with Jentek Sensors to investigate the relationship between microstructure, thermal conductivity, and dielectric constant. (Contact: Miller, R.A., e.mail: robert.a.miller@ lerc.nasa.gov)

13. Thick Thermal Barrier Coatings for Diesel Engines

Thick thermal barrier coatings for diesel engine applications are being investigated under Army Research Laboratory (ARL)and Caterpillar, Inc. funding. The ARL program includes burner rig and pulsed laser thermal cycling, a novel dilatometry-based evaluation procedure, and oxidation studies. The coatings under development emphasize thermal expansion tailoring within the bond coat layers rather than in cermet layers. The Caterpillar program will emphasize combined thermal and mechanical loading of TBC coated test specimens to replicate the conditions in the actual engine. (Contact: Miller, R.A., e.mail: robert.a.miller@lerc.nasa.gov)

14. A Comparison of the Oxidation Kinetics of SiC and Si_3N_4

There is disagreement over the relative rates, enthalpies, and rate limiting diffusion mechanisms for oxidation of SiC and Si_3N_4. This confusion may be due in part to impurity effects. This study was aimed at clarifying some of these issues by undertaking the simultaneous oxidation of CVD SiC and Si_3N_4 in clean environments. Below 1500°C, the oxidation rate of SiC is greater than that of Si_3N_4. Because of the stronger temperature dependence of the oxidation rate of Si_3N_4, the oxidation rates become the same at about 1500°C. It was concluded that the oxidation rate of SiC is limited by the permeation of molecular oxygen through silica, while the rate-limiting step for Si_3N_4 oxidation is probably oxygen transport through an SiO_xN_y subscale. (Contact: Opila, E.J., e.mail: opila@lerc.nasa.gov and L.U.Thomas-Ogbuji@lerc.nasa.gov))

15. Oxidation of SiC in Water Vapor

SiC components have been proposed for use in combustion environments. Because all combustion environments contain water vapor, the behavior of SiC in water vapor must be understood. Several studies have been undertaken to focus on this issue and three major effects of water vapor have been found. First, water vapor enhances transport of impurities to the SiC surface. These impurities then react with the silica scale and form less protective scales. Oxide growth rates are thus enhanced. Secondly, it was found that even in the absence of impurities, water vapor enhances the growth rate of silica on SiC. This occurs because water vapor is more soluble in silica than oxygen, thus increasing the amount of oxidant which arrives at the the SiC/silica interface. Oxidation rates in water vapor/oxygen mixtures have been found to have a power law dependence on the water vapor partial pressure which varies between 0.5 and 0.85. Finally, it has been found that silica is not stable in water vapor environments, but forms volatile hydroxides and oxyhydroxides such as $Si(OH)_4$ and $SiO(OH)_2$. SiC in water vapor containing environments thus oxidizes according to paralinear kinetics. Rapid consumption rates of SiC occur as silica is formed and simultaneously volatilized. (Contact: Opila, E.J., e.mail: opila@lerc.nasa.gov)

16. Reaction of Silicon Carbide in a Synthetic Fuel-Rich Environment

The thrust of this research is to determine the effect of a simulated fuel-rich combustion environment on the durability of silicon carbide (SiC). The oxidation kinetics of a pure SiC (manufactured via chemical vapor deposition) were measured by thermogravimetric analysis in a 4% H_2 - 13% H_2O - 10% CO - 7% CO_2 - balance N_2 gas mixture flowing at 0.44 cm/s in fused quartz furnace tubes. Temperatures studied were between 1300° and 1450°C. The SiC was oxidized to form solid silica, which was in turn volatilized by formation of gaseous Si-O-H products. These two simultaneous reactions result in overall paralinear kinetics. A curve fitting technique was used to determine the linear and parabolic rate constants from the paralinear kinetic data. Volatilization of the protective silica scale results in accelerated consumption of SiC. Recession rates are estimated from the furnace data. (Contact: Fox, D.S., e.mail: Dennis.S.Fox@lerc.nasa.gov)

17. SiC Recession Due to SiO_2 Scale Volatility under Combustor Conditions

One of today's most important and challenging technological problems is the development of advanced materials and processes to design and build a new fleet of supersonic High Speed Civil Transport (HSCT) airliners. The innovative combustor designs required for HSCT engines will need high-temperature materials with long-term environmental stability. Higher combustor liner temperatures and the need for lightweight materials will require the use of advanced ceramic-matrix composites (CMC's) in hot-section components. A silicon carbide composite is the liner material of interest. One of the leading combustor design schemes requires an environment containing both oxidizing and reducing gas mixtures. These environments may affect the stability of the silica (SiO_2) scale on which SiC depends for environmental protection. A unique High Pressure Burner Rig (HPBR) was developed to simulate the combustor conditions of future gas turbine engines, and a series of tests was conducted on commercially available SiC material. These tests are intended as a feasibility study for the use of these materials in applications such as the HSCT. Linear weight loss and surface recession of the SiC was observed due to SiO_2 volatility in both fuel-lean and fuel-rich gas mixtures. These observations were compared and agreed well with thermogravimetric analysis (TGA) experiments. A strong Arrhenius-type temperature dependence exists. In addition, the secondary dependencies of pressure and gas velocity have been defined. A model was developed to enable extrapolation to points outside the experimental space of the burner rig, and in particular, to potential gas turbine engine conditions. (Contact: Robinson, R.C., e.mail: Raymond.C.Robinson@lerc.nasa.gov)

18. Corrosion Processes Involving Volatile Processes

Many high temperature corrosion processes generate volatile products in addition to condensed phase products. Examples are volatile chlorides, oxychlorides, and certain oxides and hydroxyl species. Approximately twenty years ago a unique mass spectrometer was built at NASA Lewis for sampling these volatile species directly from a one atmosphere corrosion process. This instrument is based on a free-jet expansion and formation of a well-defined molecular beam. It has been updated and used over these twenty years to sample a variety of corrosion processes. The system has been used to study a variety of chlorination processes and oxychlorination processes. The precise corrosion mechanism depends on the specific metal or ceramic, as well as the chlorine/oxygen mixture. However, three basic mechanisms have been observed: (i) Scale penetration by Cl_2 and formation of a condensed phase chloride at the metal/oxide interface (ii) Direct reaction of the oxide scale with Cl_2 and (iii) Gas phase reactions of metal chlorides with oxygen. Current work deals with volatile oxides and hydroxides of boron, silicon, chromium, aluminum, and zirconium. Available thermodynamic measurements and estimates have been collected to predict the relative importance of volatile oxides and hydroxides for these elements. Recent observations have been made of HBO_2(g) and H_3BO_3(g) in oxygen with very small amounts of water vapor, which is consistent with thermodynamic prediction. In the silica system, ~90% water vapor streams produce $Si(OH)_4$(g) and $SiO(OH)_2$(g), again consistent with the limited thermodynamic measurements and estimates for this system. These phenomena are particularly important in the application of silica protected ceramics in combustion environments, which always contain substantial amounts of water vapor. (Contact: Jacobson, N.S., e.mail: Nathan.S.Jacobson@lerc.nasa.gov)

19. Oxide Coatings Development/Environmental Durability for Silicon-Based Ceramics

The aim of this work is to evaluate the feasibility of using protective oxide coatings to enhance the environmental durability of silicon-based ceramics. Mullite coating shows excellent resistance against molten salt attack, while mullite/YSZ coating demonstrates the potential as a water vapor-resistant coating. Two U.S. patents resulted from this work. Collaboration with Allied Signal is underway to transfer the coatings technology to gas turbine engine applications. (Contact: Lee, K.N., e.mail: Kang.N.Lee@lerc.nasa.gov)

20. Oxidation of the BN Interface in Composites

Boron nitride is commonly used as a SiC fiber interface coating for in SiC fiber/SiC matrix composites. A major issue with these composites is the ease of oxidation of this interface. This study involves oxidation studies of monolithic BN and BN in model composites. Monolithic BN readily oxidizes to B_2O_3, which is attacked by even small amounts of water vapor (~10 ppm) to form HBO_x(g) species. Microstructure and impurity content appear to have dramatic effects on the oxidation behavior of monolithic BN. Model composites have been fabricated by taking chemically vapor deposited SiC, depositing a layer of BN, and then a final layer of SiC. This creates a sandwich with BN in the middle. Grinding one face exposes the BN for oxidation. At the high temperatures (900°C and above) the BN remains remarkably intact. It appears that the SiC oxidizes preferentially. This getters the oxygen and lowers the oxygen potential so that the BN is stable. At lower temperatures, water vapor attack and volatilitization may be more important. (Contact: Jacobson, N.S., e.mail: Nathan.S.Jacobson@lerc.nasa.gov)

21. Sea Salt Hot Corrosion of a Silicon Nitride in a Pressurized Burner Rig

The thrust of this research is to determine the effect of sea salt in a combustion environment on the corrosion and mechanical properties of silicon nitride (Si_3N_4). A commercially available, hot isostatically pressed Si_3N_4 containing four weight percent yttria was exposed to 982°C for up to 75 hours in a burner rig pressurized to 500 kPa (5 atmospheres). Synthetic sea salt added to the flame (five ppm) resulted in formation of a sodium magnesium silicate corrosion product. A 33% reduction in room-temperature strength occurred after five hours exposure. This is thought to be due to modification of the near-surface grain boundary phase and relief of surface compressive stresses. Exposures to longer times resulted in continued strength reduction, up to 46% at 75 hours. Strength also decreased when salt concentration was increased, as shown by exposures using two and 10 ppm sea salt. In tests at 100 and 300 kPa with other variables held constant, post-corrosion strengths were similar to those after 500 kPa exposure. If this material is to be used in severely corrosive environments, protective coatings, or inlet air filtration, are needed. (Contact: Fox, D.S., e.mail: Dennis.S.Fox@lerc.nasa.gov)

22. Molten Salt Corrosion of Ceramics

Fundamental studies of the degradation of silicon-based ceramics (SiC, Si_3N_4, composites, and $MoSi_2$) and oxide ceramics are aimed at understanding the basic mechanisms of corrosion. For the silica-protected materials, basic molten salts tend to readily flux the protective film. In a continuous deposition situation, this can lead to substantial $Na_2O.x(SiO_2)$ formation and consumption of the material. Secondary elements, such as carbon and the molybdenum in $MoSi_2$, tend to alter the basicity of the salt deposit. The carbon effect is quite substantial. We have found excess carbon in SiC can drive an acidic salt deposit basic, leading to extensive attack from an otherwise non-corrosive salt. We have also found that refractory oxide coatings of silicon-based materials offer some protection in a corrosive environment. Recent studies on mullite show the behavior of mullite can be interpreted with the aid of diffusion paths in the Na_2O-SiO_2-Al_2O_3 phase diagram. In general, sodium aluminum silicates form, which are higher melting than sodium silicate. The solid sodium aluminum silicates have lower oxygen permeability and the overall corrosion is much less. However, over time, sodium diffuses through the mullite and attacks the silicon-based ceramic. Thus other refractory coatings are needed which show less permeability to sodium. (Contact: Jacobson, N.S., e.mail: Nathan.S.Jacobson@lerc.nasa.gov)

RECENT PUBLICATIONS

1. Alumina Scale Adhesion and Low Sulfur Superalloys

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Scientific Key Words: Alumina; Ceramic coatings; Chromia/alumina adhesion; Coated and uncoated superalloys; Combustion chemical vapor deposition; Oxide overlayers; Reactive element effect; Refractory metals and components; Silica coatings; Surface modification/coating; Thermal barrier coatings

Technical Key Words: Thermal barrier coating systems; Engine applications

SCOPE OF RESEARCH

Surface modifications are used to investigate the role of ‘reactive elements’ and other effects on the oxidation resistance of alloys. The methods of surface modification include both ion implantation and a new form of chemical vapor deposition (CVD), entitled combustion CVD. Examples of systems investigated include yttrium ion implantation into Ni-20Cr, aluminum ion implantation into refractory metals, and silica and alumina ceramic coatings applied to Ni-20Cr. Potential applications of the surface applied oxide coatings include thermal barrier coating systems, as well as other high temperature oxidation and corrosion areas. The abstracts which follow briefly describe the research areas:

Specific Topics

1. Aluminum Ion Implantation into Refractory Metals

This research is considered complete, and investigated the considerable improvement in oxidation that is observed upon aluminum ion implantation into tantalum, vanadium and niobium to high aluminum concentrations. It was supported by the National Science Foundation under Grant No. DMR 9102986.

2. Improvements to Thermal Barrier Coating Systems

Research is currently under way concerning the effects of applying certain ceramic materials to thermal barrier coating systems as ‘interlay’ coatings, between oxidation resistant bond coat and ceramic top coat, and as ‘overlay’ coatings, on top of the insulating ceramic. The aim is to improve the lifetime of thermal barrier coating systems by modifying the chemistry of the interfaces. This research is supported by the U.S. Department of Energy, Morgantown Energy Technology Center, Cooperative Agreement DE-FC21-92MC29061.

3. Reactive Element Effect in Alumina-Forming Systems

A five-year research program, commenced in 1996, concerns coatings for high temperature alloys. Several fundamental issues are under investigation, including the ‘reactive element’ effect for alumina-forming high temperature alloys. The combustion CVD ceramic coating technique is an integral part of this research effort, which is funded by the National Science Foundation under Grant No. DMR 9624927.

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Scientific Key Words: Carbon-carbon composite; Environmental SEM; In-situ stress measurement; Oxidation/sulfidation; Reactive element effect; Scanning transmission electron microscopy; Superalloys; Transmission electron microscopy; Titanium alloys/aluminides; Zirconium alloys

Technical Key Words: Airframe materials; Aeroengines; Coal-fired turbines; Coal gasification; Engine materials; Gas turbines; Prosthetic implant coatings

SCOPE OF RESEARCH

Fundamental Approach

The focus of the overall research program is on the fundamental science of scale microstructural development and scaling mechanisms during high-temperature oxidation and sulfidation of metal alloys and protected carbon composites. The effort has long emphasized the application of transmission (TEM) and scanning transmission (STEM) electron microscopy; high-resolution scanning (HRSEM) and environmental scanning electron microscopy (ESEM); and associated analytical techniques (X-ray energy-dispersive spectroscopy, electron energy-loss spectroscopy) to microstructural and microchemical investigations as a complement to the more conventional techniques of thermogravimetry and X-ray diffraction. The X-ray diffraction measurements routines include glancing-angle methods and high-temperature *in-situ* stress measurements in growing scales, and TEM/STEM/SEM-based elemental analysis is complemented by SIMS profiling through scales, including use of oxidant isotope-changes to identify the diffusing species rate-limiting scaling kinetics. Product scales investigated include nickel, chromium, aluminum, titanium and zirconium oxides; iron chromium and niobium sulfides; and aluminum and titanium nitrides and oxynitrides. These form on a range of alloy systems of potential industrial interest, including high-temperature Ni- and Fe-based (NiCrAl, FeCrAl) superalloys, (with and without reactive-element oxide dispersion additions), Nb-Cr binary alloys, Ti-Al-Nb alloys, and Zr-Nb alloys. A more recent program seeks to engineer oxidation protection of carbon-carbon composites using refractory metal infiltration.

Practical Applications, Engineering Achievements and Technology Transfer

The research carried out intends eventual application in turbine technologies, materials used in coal gasification plant and in other mixed oxidant environments, and in aerospace propulsion and structural materials systems. The patent on Nb-Cr alloy coatings for combined oxidation- sulfidation environments has evinced interest from quarters far beyond those envisaged in the intended applications. A promising cross-over has been made in applying high-temperature oxidation science to generate superior coatings for orthopaedic applications.

Specific Topics

1. Oxidation-Sulfidation of Refractory Metal Alloys

Materials in coal gasification are subjected to environments containing high sulfur pressures and low oxygen pressures. Materials which exhibit simultaneous oxidation and sulfidation resistance are required in those and other applications. Binary alloys, containing one component which forms a protective oxide together with a second element which is itself sulfidation resistant, appear the simplest approach to finding materials which exhibit satisfactory behavior when exposed to both oxygen and sulfur. The chromium-niobium system has been selected initially to evaluate such mixed oxidant resistance. Various Cr-Nb binary and ternary alloy compositions have been studied to evaluate mixed oxidant performance in combinations of H_2, H_2O and H_2S gases at 800-900°C and compared to elemental Cr and Nb. Pure sulfidation experiments at low PS_2 were conducted with H_2-H_2S mixtures to study alloys in extreme conditions. This work is sponsored by the U.S. National Science Foundation and the John F. Elliott Chair.

2. Reactive-Element Effect in the Oxidation of Alumina Formers

Additions of certain oxygen-active elements, such as Y and Zr, are found to promote enhanced adhesion and slower growth of high-temperature oxidation scales on Cr- and Al-containing alloys. The focus of this ongoing collaborative program with Dr. Bruce Pint (now at Oak Ridge National Laboratory) is to understand the basic mechanisms underlying this so-called reactive element (RE) effect in the high-temperature oxidation of alumina-forming alloys. Alloys studied include nickel aluminides (β-NiAl and Ni_3Al), Fe-10wt%Cr-10wt%Al alloys fabricated in the laboratory by mechanically alloying with a range of ZrO_2, Y_2O_3, Yb_2O_3, La_2O_3 and CeO_2 dispersed oxide additions, and (through additional collaborations with KFA Jülich) Fe-20wt%Cr-10wt%Al alloys with Y and Si alloy additions, oxidized at temperatures between 1273 K and 1773 K. Principal investigative tools used, in addition to thermogravimetric measurements, are isotopic oxygen profiling by SIMS, glancing-angle X-ray diffraction, SEM, TEM and analytical STEM. This research has been supported by the Electric Power Research Institute, the John F. Elliott Chair and Oak Ridge National Laboratory.

3. High Temperature Environmental Degradation of Intermetallic Aluminides

In this project, the high-temperature surface oxide scales forming on aluminide intermetallics are being studied, with a focus on the three Ti-aluminide alloys TiAl (γ), Ti_3Al (α_2) and Ti-25Al-23.5Nb (super-α_2) in the temperature range 700-800°C, as part of a larger effort in developing intermetallic compounds for a variety of high-temperature applications in gas turbine engines and airframe structures in advanced aircraft. Long-term isothermal oxidation experiments have been conducted on these three alloys in a variety of gaseous environments (dry air, pure oxygen, argon-oxygen and nitrogen-oxidation gas mixtures) and the oxidation kinetics to 100 hours determined by thermogravimetry. Glancing-angle X-ray diffraction, environmental SEM/XEDS and analytical STEM/XEDS have been used to characterize oxide morphologies, microstructures, chemistries and phase distributions. At 700°C, the super-α_2 alloy competes favourably with γ-TiAl, but the oxide formed in air is particularly complex, with repeating multilayers of Ti, Al and Nb oxides and oxynitrides with nitrogen enrichment at the scale/substrate interface. This research is sponsored by the U.S. Air Force Office of Scientific Research.

4. Stress Measurements in Oxidation Scales and Substrates

High-temperature oxidation scales growing on metal substrates sustain growth stresses, generated even during isothermal scale growth, and thermal stresses occasioned by differential thermal contact between scale and substrate during subsequent cooling or thermal cycling. These stresses can result in buckling and detachment of the scale and scale fracture, exposing the underlying substrate to renewed oxidation. In order to separate measurement of growth and thermal stresses, *in-situ* measurements are made at temperatures up to 1400°C in a hot cell installed on a precision X-ray diffractometer operating in reflection geometry. Stress measurements have now been made for the systems NiO/Ni, Cr_2O_3/Cr, NiO/Cr_2O_3/Ni-Cr, Cr_2O_3/Ni-Cr-Al (Inco MA754) and Al_2O_3/β-NiAl and most recently for TiO_2/Al_2O_3/γ-TiAl, α_2-Ti_3Al and super-α_2 Ti-25Al-23.5Nb Ti-Al aluminide alloys and ZrO_2/Zr-2.5wt%Nb.

Measured growth stresses are surprisingly high (up to 2GPa) and often of opposite sign to the differential thermal stresses imposed on cooling. This research is jointly supported by the U.S. Air-Force Office of Scientific Research and the Brigham & Women's Orthopaedic Foundation, through a grant from Smith & Nephew Orthopaedics.

5. Study of Zirconium Oxide-Zirconium Alloy Interfaces in Joint Arthroplastry Applications

Integral zirconia surface layers produced by oxidation of Zr-2.5wt%Nb substrates have been shown to provide advantageous wear resistance in articulation against ultrahigh molecular weight poly(ethylene) compared to other bearing surfaces used in total joint arthroplasties, such as bare Co-Cr-Mo alloy, oxidized Ti alloy, or TiN or diamond-like carbon deposited layers. A study of the morphological development of scale and interface by transmission electron microscopy (TEM) has been mounted, borrowing techniques developed for preparing cross-sectional thin sections in the other oxidation studies. Bone-bonding to the oxide in cementless implants is being studied by *in vivo* implants into canine models. This research is supported by the Brigham & Women's Orthopaedic Foundation, through a grant from Smith & Nephew Orthopaedics, and by Coatings Industries (Lyon, France).

6. High-Temperature Oxidation Protection for Carbon Fiber/Carbon Matrix Composites

Significant improvements in vehicle performance for aerospace applications could be realized if engine and structural components could be made from strong, lightweight materials which can operate in oxidizing atmospheres at temperatures of 1600-2000°C. Refractory carbon fibers in a carbon matrix (C-C composites) possess the necessary intrinsic strength-to-weight ratio, high-temperature stability, manufacturing ease and potential low cost to serve as structural materials in such applications but oxidize catastrophically at high temperatures and must be protected. An alternative approach to current silica-based coatings is being explored, which involves a duplex coating of $La_2Hf_2O_7$ over an Ir or Rh layer infiltrating the composite near-surface to provide a carbon-fiber-reinforced internal diffusion barrier. Infiltration is accomplished by selective oxidation of the carbon matrix phase, followed by electroplating of the carbon fiber weave with Rh or Ir from aqueous solutions with an intervening fiber coating of Re or TiC to provide wetting. The processing technology is being presently explored and the results evaluated using thin-film X-ray diffraction stress measurements, electron microscopy of the resulting microstructures, and determination of high-temperature oxidation kinetics for the coated composites. This research is a collaborative program with Pemsler, J.P., Dr., and Castle Technologies, Inc., Lexington, MA and is supported by the U.S. Office of Naval Research.

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Scientific Key Words: Chromia/alumina adhesion; Cracking/delamination; Oxide-metal interface; Interfacial fracture resistance; Stress measurement; Sulfur segregation; Scanning Auger microscopy; Reactive element effect; Erosion-corrosion

Technical Key Words: Fluidized-bed combustor; Solid oxide fuel cells

SCOPE OF RESEARCH

Fundamental Approach

The main thrust of the research is to address the problem of scale spallation on model alloys whose compositions resemble those of commercial alloys used in high temperature operations. Methods of evaluating interfacial fracture energies are evaluated, and appropriate techniques are developed and applied to each oxide/alloy system, in order to obtain a quantitative assessment of the adhesive property of the scale and its substrate. Residual stresses are determined and their effect on scale fracture and delamination evaluated. The segregation of impurities from the alloy to the scale/alloy interface and its possible effect on scale adhesion is also investigated. Apart from these studies, work is being carried out to examine the erosion and wear behavior of in-bed, heat-exchanger tubes in a simulated fluidized bed reactor. Also, the feasibility of using chromia-forming alloys as interconnect materials for medium temperature solid oxide fuel cells is being explored.

Applications, Engineering Achievements and Technology Transfer

The research is largely fundamental in nature. However, since oxide scales serve as protective coatings against further oxidation on the surface of heat-resistant alloys, the understanding of how they fail is of critical importance. Studies carried out in the simulated fluidized bed combustor have resulted in a considerable improvement in the understanding of the wastage processes of in-bed tubes under FBC systems. More direct applications are expected from the solid oxide fuel cell studies that are currently under way.

Specific Topics

1. Spallation Resistance of Thermally Grown Oxide Scales

Collaborator: Dr. Rowland Cannon of LBNL.

The resistance of oxide scales to spalling depends not only on the intrinsic strength of the oxide and of the oxide-metal interface but more importantly on the development of flaws, such as cracks, pores, or local separations of the interface. The evolution of the interface morphology during scale growth, and the segregation or collection of impurities from the metal at the moving interface, are also important factors. This work investigates ways of measuring interfacial fracture resistance of oxide/metal systems using the knowledge and techniques that have been developed in recent years on the fracture mechanics of thin films. Residual stresses in the oxide films are determined conjointly using X-ray diffraction. The goal is to understand the fracture behavior of oxide scales in relation to the oxidation mechanism and to the generation and relieve of stresses in the oxide/substrate system. Model systems of NiO grown on different purities of Ni have been studied. The next stage focuses on Cr_2O_3 scales grown on Cr, Ni-Cr and Fe-Cr alloys.

2. Mechanically Reliable Surface Oxides and Coatings for High-Temperature Corrosion Resistance

Collaborators: Drs. Ian Brown and Rowland Cannon of LBNL, and others from Oak Ridge, Argonne and Idaho Engineering National Laboratories.

This work focuses on the adherence of alumina films, formed either by the thermal oxidation of heat-resistant alloys, or by direct coating applied onto them. The coating process is achieved by a plasma immersion technique, where up to 2 µm of near stoichiometric, amorphous Al_2O_3 film can be deposited. Evolution of the Al_2O_3/alloy interface is studied using scanning Auger microscopy, scanning electron microscopy and atomic force microscopy. Detailed cross-sectional observations using transmission electron microscopy are being carried out at ORNL. These chemical and structural changes are related to oxide decohesion and spallation behaviors. In conjunction, residual stress measurements using Ruby florescence and modeling of these stresses using finite element analysis are done at ANL and INEL respectively. The goal of the combined efforts is to understand alumina scale adherence and the various factors affecting it, such that more damage-tolerant coatings can be developed. The alloys used so far are mainly Fe_3Al-based iron aluminides, with or without a Zr addition. Ni-based alloys resembling commercial superalloy compositions will be studied next.

3. Controlled Simulation of Heat Exchanger Tube Wear in Fluidized Bed Combustors

Collaborator: Dr. John Stringer of EPRI.

The wastage of heat-exchanger tubes in fluidized bed combustors (FBCs) for utility generation has been a problem of intense interest. In order to understand its mechanism and to identify the importance of various parameters involved, a unique laboratory rig was designed and built at LBNL, which simulates conditions resembling dense particle impacts on tube bottoms. In the past, the rig has proved to reflect closely situations found in operating FBCs, and insightful results regarding the mechanism of wastage have been produced. The purpose of the present stage of work is to address the effect of chlorine, in the form of HCl, on tube wastage. The goal is to identify clearly the effect, if any, and relate it to the concentration of HCl and to the specimen and bed temperatures.

4. Thin Film Electrolytes for Reduced Temperature Solid Oxide Fuel Cells

Collaborator: Dr. Steven Visco of LBNL.

The overall purpose of this project is to explore the feasibility of using oxidation-resistant alloys as interconnects for thin-film electrolyte solid oxide fuel cells (SOFCs), which have been successfully developed at LBNL in recent years. The ability of the alloy to form a protective oxide layer, the change in electrical conductivity as a result of oxide formation and the effect of different surface coatings in enhancing performance are examined. The goal is to gain a fundamental understanding of the nature of oxide scales formed at metal alloy/fuel cell electrode interfaces under conditions encountered in the operation of intermediate temperature SOFCs. Through these detailed studies, ways of improving component conductivity and lifetime may be realized that would permit commercial usage of such devices.

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Technical Key Words: Microelectronics; Electrical resistors; Resistance-change microsensors; Electrical capacitors; Surface engineering

SCOPE OF RESEARCH

Understanding the stability of thin films of refractory materials and silicides deposited on various engineering materials is the main goal of this research. The role of various surface oxides in the protection of the thin-films, hence the stability, has been an aspect of this research. The oxide-scale development process and the transport mechanisms that contribute to oxide scale growth are part of this research. The protection offered by reactively sputter-deposited oxide thin films is another area of this research. The effects that exposures to various processing chemicals, characteristic of microelectronics processing, have on the oxidation and the protective nature of the oxide scale are also included in this program. The research also addresses the interfacial stability of the thin films and the substrate. Novel methods had been developed that allowed for analyzing the interfacial reactions and the stability of the interface. The nanoscale dimensions of these films dictated that the oxidation processes be monitored by non-traditional methods, mostly electrical.

Applications, Engineering Achievements and Technology Transfer

The development of high performance thin film resistors and capacitors in high reliability applications provided the impetus for performing fundamental studies in the oxidation of TaN, Ta_2N, $TaSi_2$, Ta_2Si, $CrSi_2$, and Nichrome thin films. Films deposited on alumina, aluminum nitride, and polymeric substrates, by sputter deposition under various atmospheres, have been studied. The polymeric substrates limited the oxidation studies to 400°C; for the ceramic substrates, the temperature has been limited to 550°C.

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SCOPE OF RESEARCH

Studies of semiconductor surface electronic passivation are in progress.

In order to use semiconductor surfaces for the fabrication of integrated circuits (IC's), the surface must be electronically passivated, which requires that the surface electronic states (about $10^{15}cm^{-2}$ for most semiconductors) be reduced significantly below the level of carriers that are necessary for device applications (about $10^{12}cm^{-2}$), which are usually metal oxide semiconductor field effect transistors (MOSFETS). Electronic passivation is accomplished by the formation of dielectric films on the semiconductor surface. Film formation can be accomplished by growth or deposition and includes nucleation, coalescence and thickening. Film formation studies, particularly dielectric films, comprise a major portion of our research. The films used for IC's are usually quite thin in the active device regions and, as devices get smaller, the electronic scaling laws require even thinner films. Present technology for advanced IC's requires dielectric films less than 10 nm, and also requires special vacuum processing hardware with sensitive surface and film monitoring. The group specializes in-situ real time and spectroscopic ellipsometry, which enables the following of film formation kinetics from the nucleation stage forward and in thermal and plasma environments. The evolution of surface roughness and morphology using atomic force microscopy, composition using x-ray photoelectron spectroscopy, and structural aspects using transmission electron microscopy are also studied. It is endeavored to correlate the materials properties and film formation kinetics with interfacial electronic properties, which include capacitance and current versus voltage and electron tunneling measurements.

Applications, Engineering Achievements and Technology Transfer

The rates of growth of dielectric films provide process engineers with process design data. The correlations of kinetics, materials and electronics properties also provide process engineers with process design parameters. Over the years, ellipsometry has been developed by the group for use in characterizing processes and materials and recently an electron tunneling measurement has been employed to access the thickness of 5nm films more accurately than has been done previously. Many of the data and techniques are in practice in microelectronics processes. The following includes abstracts of our main ongoing projects.

Specific Topics

1. *Passivation of Si, Ge, InP and GaAs Surfaces Using Electron Cyclotron Resonance Plasma Growth and Deposition of Dielectric Films*

This research compares the four major semiconductor surfaces with each other and with similar studies using purely thermal processes. The nature of the films produced in plasmas and thermally are also compared and the resulting electronics passivation capabilities are measured. In-situ real time ellipsometry studies in the plasma environment elucidate the kinetics of film formation as well as optical properties.

2. *Si Nucleation on SiO_2 Studies*

In-situ, real time ellipsometry is used to follow the initial nucleation stage for the formation of Si on SiO_2 surfaces. The ability to control nucleation enables selective film formation, that is, film formation where one desires a film and nowhere else. Total success with selective deposition obviates lithography which is a costly process step. The studies are carried out in a rapid thermal processing system.

3. *Roughness Evolution During Si Oxidation*

Purposely roughened and smooth Si surface are oxidized both thermally and in plasmas and the surface roughness is evaluated using atomic force microscopy. The roughness is evaluated using both statistical scale dependent parameters such as RMS roughness and the Fractal dimension which measures the complexity of the roughness. Smoothing of roughened surfaces and roughening of smooth surfaces have been observed. Models for the phenomena are presently being developed using thermodynamic and kinetic driving forces.

4. Fowler-Nordheim Tunneling Current Oscillations Studies of Ultra Thin Dielectric Films

The FN tunneling current oscillation technique has been developed in the group to measure SiO_2 film thicknesses for less than 5 nm films to 0.1nm accuracy. Presently, the technique is being employed to measure the reliability of ultra thin oxide films and metal-oxide interfaces in addition to Si-oxide interfaces.

5. Growth and Characterization of High Temperature Superconductor Films

Ion sputtering is being used to prepare $YB_2Cu_3O_{7-*}$ (123HTSC) high temperature superconductor films. In a unique configuration we also use time of flight ion scattering and recoil spectroscopy (ToF-ISARS) and in-situ ellipsometry for real time compositional and kinetics studies during film formation. For 123HTSC the amount and atomic position of O is key in determining the Tc and O can be measured directly using both ToF-ISARS and ellipsometry. This work is collaborative with scientists at Argonne National Laboratory (Auciello, O. and Krauss, A.R.).

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Technical Key Words:	Coal gasification; Entrained bed gasifier; Oxygen-blown gasifier; Syngas coolers; Petrochemical industry; Refining; Ethylene pyrolysis; Fossil fuel fired equipment

SCOPE OF RESEARCH

Fundamental Approach

The research objective is to identify the maximum allowable conditions for successful economic use of alloys in high temperature process equipment. This is accomplished by identifying critical parameters in high temperature gases which define the corrosion behaviors and corrosion rates of commercial alloys in current industrial processes. Many alloys in current use today have not been well evaluated in terms of how the structural thickness of components can be reduced by corrosion, which can be influenced by high temperature corrosive gases present in many processes. Examples of these processes are found in energy systems, petroleum processing, petrochemical manufacturing, and fossil fuel fired equipment. The data available in literature and the data generated by the studies in these programs are being brought to a common basis of comparison, which is the maximum total metal penetration. Total metal penetration is defined as the sum of sound metal lost by surface scale formation plus internal corrosion. These types of corrosion data are being correlated with well defined exposure conditions in order to produce correlation equations which can be used to predict corrosion for a wide variations in parameters such as temperature, time, and gas composition characteristics (depending upon the prevailing corrosion mechanism). For example:

- oxygen partial pressure is determined for oxidation,
- oxygen and sulfur partial pressures are determined for sulfidation/oxidation,
- carbon activity and hydrogen sulfide partial pressure are determined for carburization,
- hydrogen sulfide and hydrogen partial pressures are determined for sulfidation.

Applications, Engineering Achievements and Technology Transfer

The research effort is aimed at producing reliable and accurate corrosion predictions of commercial alloys exposed to wide ranges of process conditions in diverse equipment. The transfer of technology has included: (a) publishing the results in an industry symposium to distribute the information and concepts being developed, including proposal on how corrosion data should be measured; (b) guiding the development of a best practice for assessing the carburization behavior of heat resistant alloys; (c) educating alloy supply companies with respect to preferred data reporting approaches; (d) distributing the ASSET software throughout Shell for the purpose of predicting/assessing high temperature corrosion of metals and alloys used in various items of high temperature process equipment, and (e) considering a public, collaborative program to enhance and distribute the ASSET program to other companies. High temperature alloy corrosion data suitable for inclusion in the ASSET data bases are welcome.

Specific Topics

1. Corrosion in Sulfidizing-Oxidizing Gases in Coal Gasification Equipment

This research was performed to evaluate the corrosion behavior and rates of alloys exposed to conditions simulating conditions expected in an entrained bed coal gasification process, several oil refining processes which handle H_2-H_2O-H_2S gases at high temperatures, enhanced oil recovery processes, and oil gasification.

2. Carburization of Heat Resistant Alloys

This effort was aimed at improving the understanding of how test conditions used by alloy suppliers to evaluate carburization behavior of heat resistant alloys influence the carburization test results. This effort has continued with a project by the Materials Technology Institute which has sponsored a project to define a best practice for carburization testing.

3. *High Temperature Oxidation*

This research evaluated the oxidation behavior of commercially available alloys in conditions simulating fossil fuel-fired equipment and showed that traditional data which often report only weight change/unit area in fact reports typically only 10-20% of the total sound metal loss caused by oxidation. Addition of the thickness of metal loss by internal oxidation to the metal loss by surface scale formation yields a total metal penetration, which is the information of most interest to equipment operators and designers.

4. *Compilation, Analysis, and Utilization of Data on Alloy Corrosion in High Temperature Gases*

This project has compiled a large collection of high temperature corrosion data for alloys corroding by oxidation, sulfidation, sulfidation/oxidation, carburization, sulfuric/sulfurous acid dew point corrosion, and cyclic oxidation. The data have been organized into a Windows program using Microsoft Access in a manner to allow generation of quantitative correlations between corrosion exposure conditions for the first four mechanisms listed previously. The data collection represents 4.7 million hours of exposure for a total of 71 alloys. The ASSET (Alloy Selection System for Elevated Temperatures) program archives data, correlates corrosion with exposure conditions, predicts corrosion for specified conditions, and determines the stable alloy corrosion products. There is some consideration of a public, collaborative effort to enhance and distribute the ASSET software.

RECENT PUBLICATIONS

1. Corrosion in Sulfidizing-Oxidizing Gases in Coal Gasification Equipment

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4. Compilation, Analysis, and Utilization of Data on Alloy Corrosion in High Temperature Gases

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Scientific Key Words: Corrosion; Life prediction; Ceramic coatings; Coating methods; Computer modeling; Corrosion fatigue; Crack growth; Electrochemical measurements; Electrochemical sensors; H2 sensors; High temperature water corrosion; Lifetime; Mathematical modeling; Modeling diffusion/ multicomponent systems; Monitoring; Nickel alloys; pH monitoring; Pitting; Passivity; Sensors; Thermodynamic modeling; Thermodynamic stability diagrams; Water; Water chemistry sensors; Advanced batteries; Microbially-induced corrosion

Technical Key Words: Steam boiler; Ultra-supercritical plant; Nuclear power systems; Steam generators; Electrochemical Sensors

SCOPE OF RESEARCH

Fundamental Approach

The Center for Advanced Materials (CAM) is a multidisciplinary materials research center located in the College of Earth and Mineral Sciences. The current and recent past sponsors include government agencies (DOE, NASA, ARO, ONR), industry (GRI, EPRI, DuPont, Mobil), and international organizations (IHI, KEPCO, MHI, UEF, IAPWS). The work now ranges from exploring fundamental corrosion and electrochemical phenomena under extreme environmental conditions (e.g., in high subcritical and supercritical aqueous systems), exploring the growth and breakdown of passive films on metal surfaces, modeling the development of damage, simulating environment-assisted fracture and other forms of localized corrosion, battery science and technology, and modeling the electrochemistry of water-cooled fossil and nuclear power reactor coolant circuits. Recently, a damage prediction code has been developed that allows an operator of a boiling water reactor (BWR) or a pressurized water reactor (PWR) to obtain detailed and vital information on the electrochemical properties (ECP) and crack growth rate for any given set of plant operating parameters. The theoretical predictions depend critically on the values of a number of parameters that describe, or arise from, various physico-chemical processes that occur in the system. Because most of there parameters are not accessible theoretically, they must be derived experimentally. A principal task of the Center is to measure kinetic parameters, including exchange current densities and Tafel constants, for the reactions that occur on the external surfaces of alloys in high temperature aqueous systems that are used extensively in industrial and military-related systems. For example, subcritical and supercritical aqueous solutions are used in electrical power generating facilities, including nuclear power reactors. Furthermore, supercritical water oxidation (SCWO) is being developed intensively as a means of destroying toxic waste and for treating low-level rad waste from various DOE operations. CAM has been a leader in developing the fundamental basis of SCWO through support from ARO, DOE/INEL, and DOE's Environmental Management Program and the Center started to develop a unique data base of thermodynamic properties of aqueous solutions in high subcritical and supercritical conditions. This data base is urgently needed for engineering calculations of SCWO processes and power plant industry.

Applications, Engineering Achievements and Technology Transfer

The Nuclear Power Industry loses billions of dollars each year through unscheduled outages, many of which are due to stress corrosion cracking (SCC) and corrosion fatigue (CF). Work carried out in the Center for Advanced Materials and elsewhere has shown that the electrochemistry of the system and the chemistry of the water are major factors in determining the susceptibility of steels to SCC and CF in power plant coolant circuits. Many outages could be prevented through more efficient chemistry control, which requires advanced chemistry and corrosion simulation and monitoring technologies. The Center has developed techniques to simulate coolant electrochemistry and component corrosion in Boiling Water Reactor and Pressurized Water Reactor coolant circuits. Techniques for measuring pH, ECP, dissolved hydrogen, etc. have been devised and are now being employed in power plant coolant systems.

Specific Topics

1. Corrosion Potential Measurements and Modeling of Simulated PWR Steam Generator Secondary Environments

This work is sponsored by Electric Power Research Institute. A new, Coupled Environment Crevice Model (CECM) model for describing transport processes in SG tube/support plate cavities has been developed. The model allows one to predict the solution chemistry, potential distribution, and corrosion rate inside the cavity under non steady-state conditions. In spite of the complexity of the problem, a simple (but accurate) analytical method for calculating the average volume concentrations of impurities and corrosion products in the cavity has been devised. An apparatus for investigating electrochemical and corrosion phenomena in boiling crevices was constructed to test the CECM and preliminary data show that the model is capable of accounting for the crevice properties under plant operating conditions.

2. Development of an Advanced External Reference Electrode for Accurate pH, Potentiometric, and Corrosion Studies at Temperatures up to 400°C

This work is sponsored by Electric Power Research Institute. A new, flow-through external pressure-balanced reference electrode has been developed for potentiometric and pH measurements in high temperature aqueous solutions. Highly accurate potentiometric measurements can be carried out using this electrode, because the electrolyte concentration profile in the liquid junction is maintained constant and the associated uncertainty in the thermal liquid junction potential can be eliminated at a given temperature and pressure.

3. Evaluation of Advanced Mitigation Techniques for BWR Internals

This work is sponsored by Electric Power Research Institute. The heterogeneous inhibition of redox reactions (O_2 reduction, H_2O_2 reduction, and H_2 oxidation) on surfaces external to the crack is being explored as a strategy for mitigating stress corrosion cracking in sensitized Type 304SS in simulated BWR heat transport environments. Sensitized type 304 stainless steel specimens and samples were coated entirely with an adherent dielectric layer of ZrO_2 via electrophoretic deposition. Constant load SCC tests were performed on the specimens under simulated BWR conditions, and inhibition of crack growth has been demonstrated. The coatings were characterized using electrochemical impedance spectroscopy.

4. *Development of Immobilized Electrolyte Reference Electrodes for High Temperature Aqueous Systems*

This work is sponsored by E. I. du Pont de Nemours and Company, DuPont Central Research and Development. A number of potentiometric sensors have recently been developed for monitoring the chemistry of aqueous systems under subcritical and supercritical conditions. For these electrodes to be truly accurate, they must be used in conjunction with a stable reference electrode. The goal of this research is to design an immobilized electrolyte reference electrode that does not exhibit drift in the reference potential at high temperatures due to thermal diffusion.

5. *Investigation of the Kinetics of Passivation of Nickel Base Alloys Using a Dropping Weight Method*

The objective of this work is to obtain fundamental repassivation kinetic data for nickel based alloys that may be used for modeling stress corrosion cracking in high temperature aqueous environments. The experiments are being performed in aqueous solutions at temperatures up to 360°C.

6. *Exploration of the Electrochemical and Corrosion Behavior of Steels and Nickel-Based Alloys in Sulfur-Containing Environments*

A data base of thermodynamic and kinetic parameters is being developed that can be used by corrosion scientists and engineers to interpret the corrosion of nickel-based alloys and steels in high temperature aqueous systems in laboratory experiments and in field studies. A high temperature electrochemical test cell has been designed for exploring corrosion phenomena on nickel-based alloy in sulfur-containing aqueous environments at temperatures up to 300°C under controlled hydrodynamics/mass transport conditions.

7. *Characterization of Galvanic Coupling Between Chromium Carbides and Fe-Cr-Ni Alloys*

Characterization of galvanic coupling between various metallurgical phases in Ni-Cr-Fe alloys in aqueous environments at temperatures up to 300°C, using state-of-the-art electrochemical techniques, is being carried out. The principal objective is to ascertain the anode/cathode relationships between different phases in an alloy when exposed to high temperature water.

8. *Development of Advanced* In Situ *Techniques for Chemistry Monitoring and Corrosion Mitigation in SCWO Environments*

This work is sponsored by the Department of Energy. Chemical and corrosion sensors for use in high subcritical (300<T<374°C) and supercritical (T>374°C) aqueous environments are being developed, with the objective of improving their precision and reliability. This work emphasizes the development of advanced reference electrodes, fabrication of pH and redox sensors, and the development of electrochemical emission spectroscopy, as means of characterizing metal/water interactions (including corrosion) processes. For example, pH has been measured at temperatures as high as 550°C and sensitive methods for measuring H_2 and O_2 *in situ* at supercritical temperatures have been devised.

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Technical Key Words: Furnace wall corrosion; Boiler tube failures; Surface engineering

SCOPE OF RESEARCH

Fundamental Approach

The major research objectives involve the study of protective coating systems, including weld overlay, thermal spray, and electrodeposited/diffusion coatings, for high temperature corrosion and solid-particle erosion environments. Recent studies have shown the effect of Cr content on the sulfidation behavior of binary Fe-Cr alloys at 600°C using a diffusion couple technique. An alternative coating technique, namely electrodeposited composite coatings with subsequent diffusion, is also being developed. Ni-Al coatings produced with this technique have shown very little attack during high temperature oxidation testing. Current research is being conducted on corrosion of several coating materials, including Fe-Al weld overlays, in a newly constructed gaseous sulifidizing or mixed sulfidizing/oxidizing thermogravimetric balance (TG). The environments are chosen to simulate corrosive attack found, for example, in low NO_x boilers for power generation. The research will involve thermogravimetric sulfidation and oxidation testing as well as long-term isothermal and cyclic corrosion testing of alloys and coatings for possible applications in low NO_x boilers. Extensive research has also been performed on solid-particle erosion of bulk alloys and coatings using a unique erosion test facility. An analysis of solid-particle erosion of cast and wrought alloys has been used to gain an understanding of the material properties affecting erosion resistance. In addition, studies of the effects of hard-phase content and morphology on the erosion behavior of bulk composites and thermal spray coatings has been conducted. Further work is under way on several alloys to develop more insight into the controlling mechanisms of erosion.

Applications, Engineering Achievements and Technology Transfer

Research at the Energy Research Center has focused on the processing, characterization, erosion, and corrosion properties of materials and coatings for application in boiler environments of the power generation industry as well as other applications. Future research will focus on sulfidation and oxidation studies in a recently constructed high temperature corrosion facility as well as continued research in the areas of processing, characterization, and erosion. Work is carried out with industrial consortia as well as government sponsorship as indicated below. Laboratory developed coating results are being correlated with field experiments in fossil fired boilers.

Specific Topics

1. *High Temperature Corrosion of Alloys, Welds, and Coatings for Fossil-Fired Boiler Applications*

Research students: K. Luer, S. Banovic

High temperature corrosion of alloys, weld overlays, and coatings for fossil-fired boiler applications is being investigated using short-term thermogravimetric techniques and long-term furnace testing. Test materials are characterized using traditional materials characterization techniques: visual examination, LOM, SEM, EPMA, and XRD. Results are also compared to field data and observations. In addition, the initial stages of high temperature oxidation and sulfidation on materials are being investigated in a dedicated environmental scanning electron microscope (ESEM).

2. *Solid Particle Erosion of Cermet-Composite Materials for Coal-Fired Power Generation*

Researchers: B.F. Levin, B.A. Lindsley

This research is supported by the U.S. Department of Energy and an industrial consortium of eight utilities. The objective is to determine the effect of mechanical properties and microstructure on the erosion resistance of metal-matrix composites. Various metal-matrix composites were produced using thermal spray, hot isostatic pressing, and electrodeposition processes. The effects of volume fraction and size of the hard second phase particles and the effect of mechanical properties on erosion resistance of metal-matrix composites are being analyzed. Erosion tests are conducted using an erosion simulator that contains a Laser Doppler Velocometer (LDV) for accurate measurement of the velocity of the impacting particles.

3. *Evaluation of Iron Aluminide Weld Overlays for Erosion-Corrosion Resistant Boiler Tube Coatings in Low NO_x Boilers*

Research student: S.W. Banovic

This research is a collaboration between the Energy Research Center at Lehigh University and Oak Ridge National Laboratory under the *Fossil Energy Advanced Research and Technology Development Materials Program.* The goal of the work is to evaluate iron-aluminum (less than 10wt% Al) alloy weld overlays produced by Gas Tungsten Arc Welding (GTAW) and Gas Metal Arc Welding (GMAW). Laboratory investigations include weldability, oxidation, sulfidation, and erosion resistance of the coatings. Simulated conditions, i.e., temperature, partial pressures of sulfur and oxygen, etc, will be representative of environments found in low NO_x boilers. Results will be compared to other candidate weld overlays and existing material systems presently used to protect water wall tubes.

4. *Electrodeposited Composite Coatings for High Temperature Corrosion Resistance*

Research student: D.F. Susan

An alternative coating technique, namely electrodeposited metal matrix/metal particle composite coatings (EMMC), is being studied using Ni matrix/Al particle coatings as a model system. Ni-Al coatings with up to 20 vol.% Al particles were deposited, heat treated, and characterized. Heat treatment at 635 and 800°C produces a two-phase structure of Ni_3Al (γ') in a (solid solution matrix with small Kirkendall voids also present. The microhardness of the coating was found to increase with increasing Ni_3Al content. The Ni-Al coatings were oxidation tested in air at 800, 900, and 1000°C for up to 900 hours. Results indicate that the Al content is sufficient to form a protective alumina scale during isothermal exposure at these temperatures.

5. *Minimizing Residual Stresses, Distortion, and Thermal Fatigue Cracking in Weld Overlay Applications*

This research is supported by an industrial consortium. A finite element model is being developed to predict residual stress and distortion patterns in weld overlay applications. Once complete, parametric studies will be conducted to investigate processing conditions which can be implemented to minimize stresses and distortion. Experimental verification is planned on both small scale and large scale overlay structures. Fatigue crack propagation experiments are being conducted to determine the inherent resistance of the brittle interfacial regions to thermal fatigue cracking.

RECENT PUBLICATIONS

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Technical Key Words: Engine materials; Waste incineration; Ceramic heat exchangers; Recuperators; Hot gas filtration

SCOPE OF RESEARCH

1. *Corrosion of Advanced Materials in Complex Industrial Environments Containing Halogens*

Advanced materials have useful properties obtained by special processing of unique materials. These materials are often used in aggressive, high-temperature environments where conventional materials are unsuitable. In some cases, their properties degrade as a result of chemical interactions with the environment. Understanding of this degradation requires a knowledge of the synthesis and fabrication technology used to fabricate the materials, and the potential interactions between the microstructure and environment. The research addresses these phenomena for advanced metals, ceramics and composites in environments involving high temperatures, complex gas mixtures, and physical phenomena including wear, thermal cycling, and fatigue. Many of the projects specifically address environments containing chlorine or other halogens and their compounds, which can damage materials which are highly resistant to attack in more common environments such as clean air Relatively small amounts of halogen contamination can have drastic effects on the kinetics of oxidation or can change the mechanism of corrosion from general attack to a more dangerous localized mode. In some cases, the halogen's effect may be benign or even beneficial to certain applications.

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SCOPE OF RESEARCH

Fundamental Approach

This research is based on the assumption that the high temperature oxidation of Nb alloys will be controlled only when oxygen diffusion in these alloys is also controlled. This project studies oxygen diffusion in two alloys that interact with oxygen in different ways. In Nb-V alloys, V atoms attract oxygen atoms, which become trapped in interstitial sites nearest to the V atoms. In Nb-Pd alloys, Pd atoms repel oxygen atoms, which now avoid the nearest-neighbor interstitial sites. Oxygen diffusivity, D_{ox}, has been measured experimentally in both systems, and a computer program has been written that simulates interstitial diffusion in both cases. These two research efforts are described in more detail on the following pages. The long-range goal of this project is to develop an oxidation-resistant Nb alloy.

Applications, Engineering Achievements and Technology Transfer

Nb alloys have high melting points, low density and good room-temperature ductility, making them especially attractive for aerospace applications. Nb-based alloys have been used for Apollo Lunar Module descent nozzles, thrusters for spacecraft attitude control systems, thrust augmentor flaps in some advanced military jet turbines, and are being considered for use in space-based nuclear reactors. However, Nb alloys have poor oxidation resistance, which hinders their use in many high-temperature applications. Oxidation-resistant coatings have been developed for these alloys, but they tend to crack and spall off upon thermal cycling. These coating-substrate systems would be less susceptible to such problems if the base alloy had better inherent oxidation resistance.

Specific Topics

1. Experimental Measurement of D_{ox} in Nb-V and Nb-Pd Alloys

Alloys containing up to 20 atomic % V or Pd are made via conventional arc melting and homogenization techniques. Oxygen diffusion takes place in a modified 'Rhines' pack': alloy samples are heat treated while embedded in NbO powder. Oxygen forms via decomposition of NbO and penetrates the sample, with no external oxidation. Since the microhardness of Nb is a direct function of its oxygen content, D_{ox} can be calculated from profiles of microhardness vs. penetration depth.

2. Computer Simulation of D_{ox} in Nb-V and Nb-Pd Alloys

The group has written a computer program that uses a random walk algorithm to simulate oxygen diffusion in Nb. The program constructs a three dimensional array representative of the lattice sites in a bcc crystal, and distributes substitutional solute atoms at random throughout this lattice. Oxygen atoms are then allowed to 'walk' through the array. The probability of an oxygen atom jumping into a site is input by the user, and depends on whether the solute attracts or repels oxygen. The correlation factor, f, is calculated from the mean-squared distance that the oxygen atom travels after repeated walks. By varying the model parameters, this program can reproduce the diffusion behavior observed experimentally.

Future Plans

The use of repeller atoms to block oxygen diffusion could be a new method for controlling interstitial diffusion in many systems besides Nb-Pd alloys. It would be particularly relevant to the study of selective oxidation in ternary Nb-Pd-M alloys. In these systems, D_{ox} could be varied by simply changing the Pd concentration until a transition from internal to external oxidation of the third component occurs. If element M forms a dense, adherent oxide layer, then the alloy is protected against further attack. Input is currently sought from any groups interested in collaborating on this research, or who may have experience in related refractory metal-noble metal alloys.

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Technical Key Words: Coal gasification; Fluidized bed combustor; Heat exchangers; Surface engineering; Land-based gas turbines

SCOPE OF RESEARCH

Fundamental Approach

The major objective of the high-temperature materials program at Argonne National Laboratory is to evaluate the performance of materials in the potentially hostile environments prevalent in coal-gasification, coal combustion systems including advanced pulverized coal-fired boilers and fluidized-bed combustion (FBC), gas turbines, and fusion reactor systems. Furthermore, the programs are conducted in a generic fashion so that the results will be useful and applicable to several coal-based energy-producing systems. The work for the fusion reactor application involves development of electrically insulating coatings on refractory metal alloys and the potential interstitial interactions between the first wall and the blanket environment. The emphasis in the programs is to develop a fundamental understanding on protective scale development, the role of hostile reactants, such as sulfur, chlorine, alkalis, sulfur sorbents, ash constituents, and interstitials such as hydrogen, carbon, and nitrogen on scale development/breakdown, interactions between corrosion and mechanical properties, and the development of coatings and surface modification via ion implantation and sputter deposition for improved corrosion resistance.

Applications, Engineering Achievements and Technology Transfer

The goals of the ongoing research programs at Argonne National Laboratory are to develop a fundamental understanding of materials and their performance in several energy systems and, based on this understanding, develop materials and/or establish envelopes for satisfactory performance of materials in the hostile environments of practical situations. Another goal is to conduct exploratory research on new materials which have the potential to improve the performance of existing materials or enable the development of new/advanced energy concepts. The programs are generic and crosscutting but the results are application oriented. Several of the programs and their specific objectives are listed below.

Specific Topics

1. Corrosion of Alloys in Sulfur-Oxygen Environments

Experimental programs are being conducted to evaluate the oxidation/sulfidation behavior of metallic alloys, with and without reactive element additions. The major emphasis in the program is to evaluate the progressive development of oxide scales in the absence and presence of sulfur in the environment. The experimental conditions cover a wide range of oxygen and sulfur partial pressures, typical of both gasification and combustion conditions and a wide temperature range.

2. Corrosion of Alloys in Chlorine-Containing Environments

Conversion of coal, especially in coal gasification and in fluidized-bed combustion systems, has resulted in the release of a significant amount of chlorine which seems to accelerate metal wastage in evaporator and superheater tubes. This program examines the role of chlorine in the mixed-gas environment, with and without sulfur, in the scale development/breakdown of structural alloys of interest for heat exchangers and gas turbines. In addition, deposits of alkali sulfates and chlorides are used to simulate the high-chlorine combustion environments.

3. Surface Modification for Improved Sulfur Resistance

Several approaches are being attempted to modify the surface regions of candidate structural alloys to improve their corrosion resistance when exposed to sulfur- and chlorine-containing environments at elevated temperature. The program includes electrospark deposition, pack diffusion, and physical vapor deposition processes. Thermogravimetric experiments are being conducted under both isothermal and thermal-cycling conditions to evaluate the potential of several modified surfaces. The post-exposure examinations of the specimens are conducted using scanning electron microscopy, electron microprobe, scanning Auger spectroscopy, and ESCA techniques.

4. Corrosion Performance of Iron Aluminides

Iron aluminides are being developed for use as structural material and/or cladding in sulfur-containing environments at elevated temperatures. Several heats of Fe aluminide with different alloying additions such as B, Nb, Zr, Mo, etc are being examined for their corrosion resistance in oxidizing, sulfidizing, and chlorination environments, as well as in mixed gas atmospheres that contain O, S, and Cl. Experiments are conducted in low- and high-oxygen environments, typical of coal gasification and coal combustion, respectively.

5. Evaluation of Ceramic Materials for Combustion Applications

Advanced combustion systems require furnaces capable of operation at temperatures higher than those possible with metallic materials. Experimental and commercial monolithic and composite ceramic materials are being tested for their resistance to oxidation, sulfidation, and slag attack in simulated combustion atmospheres. Experiments are being conducted at temperatures between 1000 and 1400°C to evaluate the effects of composition and microstructure of the ceramic on their corrosion resistance. Four-point bend tests are conducted on the corroded specimens to determine the residual flexure strength of the materials.

6. Oxidation of Refractory Alloys

Refractory alloys based on V are being considered as the first wall material in the advanced blankets of fusion reactor. The program is aimed at understanding the kinetics of uptake of interstitial such as O, H, C, and N by V-Cr-Ti alloys as a function of temperature. Further, the influence of the interstitial uptake on the mechanical and fracture properties of the materials is investigated. The ultimate goal of this program is to establish the performance envelopes for the alloys in gaseous and liquid metal environments, with a wide range of chemistries anticipated in fusion reactor systems.

7. Development of Mechanically Reliable Scales

The corrosion resistance of a structural alloy is determined by the development and maintenance of oxide scales and their protective characteristics. A majority of the alloys develop either chromia or alumina scales which impart their corrosion resistance. However, these scales tend to fail over time by both chemical and mechanical reasons and eventually the corrosion resistance of the alloys are impaired. The purpose of this program is to develop a fundamental understanding of scaling in selected model alloys at elevated temperature and to characterize the chemical, microstructural, and mechanical properties of the scales. Techniques such as ruby fluorescence, Raman spectroscopy, secondary ion mass spectroscopy, and Auger electron spectroscopy are used to characterize the scales and to determine strains that result during oxide growth and as a result of thermal expansion mismatch between the scale and substrate.

8. Development of Ultra High-Temperature Intermetallics

The exploratory program is aimed at developing intermetallic alloys with a temperature capability up to 1400°C, i.e. beyond the capability of Ni-base superalloys. Molybdenum silicide with a composition of Mo_5Si_3 is being examined for their fabrication routes, microstructural characteristics, oxidation and pesting-related issues, and the effect of oxidation on mechanical properties.

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SCOPE OF RESEARCH

Fundamental Approach

The emphasis of the research is on the performance of materials in sulphidising environments at high temperature. The overall objective is to reproduce in the laboratory the morphology of attack observed in service and to develop a capability to predict rates of degradation in service. Thus, modern analytical techniques are used to characterize corrosion attack in laboratory testspieces exposed in controlled conditions and thermochemical modeling is applied to determine phase relationships. The effects of deposits in influencing degradation behavior are being assessed.

Testpieces exposed on probes installed in boilers burning coal and biomass have been examined to determine the characteristics of attack in operating environments and the results compared with those obtained in laboratory testing.

Applications, Engineering Achievements and Technology Transfer

Testpieces of mild steel and of low alloy steels have been exposed in gaseous environments, with controlled sulphidising potentials at elevated temperatures, for times up to several thousand hours. The weight loss following exposure has been used as one method for evaluating corrosion resistance while similar testpieces have been sectioned and examined metallographically using scanning electron microscopy with EDAX and WDS analytical capabilities.

The effect of deposits in influencing corrosion attack has been evaluated using testpieces immersed in powdered coal and experiments have been performed with active carbon to establish the influence of impurities in coals on corrosion behavior. An important factor has been the evaluation of various surface protection techniques to assess the effectiveness in resisting corrosion attack in sulphidising environments and the results have confirmed that chromising will provide a high degree of protection. The work is carried out as part of an overall development program so that there is a readily available route for technology transfer.

Equipment and Recommendations

Gas blending and flow measurements are performed using mass flow meters that are checked every 500 h using a DRYCAL volumetric flow standard and the units are calibrated by the manufacturer every 3000 h. It is recommended to avoid the use of premix gases containing H_2S and CO and to request all certified specialty gases to be delivered in aluminum cylinders. Logging of gas flow, furnace temperature and exposure time are recorded continuously by interfacing with a computer using LABVIEW, with the whole testing facility being supported by an independent power generation system for uninterrupted exposures.

Collaboration

Collaboration is with Singheiser, L. Dr., and Knoedler, R., Dr., of the ABB Corporate Research Center in Heidelberg, Germany

Reporting

12 internal reports have been issued and, due to the sensitive nature of the generated data, open literature publications are scrutinized by the ABB organization with possible publications in the course of 1997.

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Scientific Key Words: Coating C-C composites; Coating durability/adhesion; Coating/modifying surfaces; Diffusion barrier; Thermal cycling

Technical Key Words: Aerospace systems; Engine materials; Future turbine blades

SCOPE OF RESEARCH

Specific Topics

1. *Carbon Fiber Reinforced Diffusion Barriers for the Protection of Carbon-Carbon Composites at 1600°-2000°C*

A novel coating to protect carbon-carbon composites (C-C) from oxidation at temperatures as high as 1600°-2000°C is being investigated. The duplex coating consists of: 1) an inner diffusion barrier of carbon fiber reinforced iridium or rhodium and: 2) an outer layer of plasma sprayed lanthanum hafnate. Carbon char is first removed by selective oxidation from the surface layers of two-dimensional C-C. The carbon fibers are not attacked and the resulting matrix-free woven fiber surface layer, typically 30-80 μm in depth, serves as host for the barrier metal. The barrier is produced electrochemically by infiltrating noble metal into the matrix-free surface layer to produce a CArbon Fiber Reinforced Internal Barrier (CAFRIB.) The CAFRIB configuration functions as a near total diffusion block to both oxygen transport inward and carbon transport outward. CAFRIB, which acts as a carbon fiber reinforced metal matrix composite, also serves to accommodate the large stresses due to the thermal expansion mismatch between C-C and the duplex coating.

Periodic current reversal techniques have been developed to infiltrate rhodium and iridium into the matrix-free carbon fiber surface layer to produce Rh-CAFRIB and Ir-CAFRIB. In Rh-CAFRIB, the CAFRIB zone is substantially filled with Rh to a depth of ~40 μm, with lesser amounts of Rh extending to ~80 μm. Samples thermally cycled to 1600°C for five cycles show no cracks or disruption of the CAFRIB zone.

Infiltration techniques will be optimized to allow preparation of substantially filled Ir-CAFRIB. Currently, it is only possible partly to fill the CAFRIB zone with Ir. Partly filled samples were successfully thermally cycled to 1800°C without cracking or loss of Ir.

Detailed studies of the oxidation behavior with thermal cycling of both Rh-CAFRIB and Ir-CAFRIB will be undertaken in future studies.

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Scientific Key Words: Chloridation; Diffusion coatings; Hot corrosion; Interphase interfaces; Mixed oxidants; Pack cementation; Reactive element effect; Silicide coatings

Technical Key Words: Coal-fired boiler; Thermal barrier coating systems; Hot gas filtration; Waste incineration

SCOPE OF RESEARCH

Fundamental Approach

The research activities involve several quite different types of experimentation (pack cementation diffusion coatings, mixed oxidant scaling/evaporation attack, hot corrosion by fused salt films, interfacial structure and dynamics), so the specific fundamental approach depends upon the subject matter. In the development of pack cementation processes for the protection of steels or refractory alloys, the thermodynamics of halide chemistry are examined to uncover methods for the codeposition of two (or more) elements in the growth of a protective diffusion coating. For example, codeposition of Cr + Si and Al + Cr to develop highly resistant ferrite surface layers on steels has been achieved. The codeposition of Si + Ge to grow Ge-doped disilicides on alloys high in Nb, Ti or Mo has provided very protective surface layers. The attack of Fe-Cr, Ni-Cr and commercial austenitic alloys in H_2-H_2O-HCl gas involves the competition between the formation of a protective oxide scale and the evaporation of volatile chlorides. Hot corrosion studies are generally interpreted in terms of the basicity-dependent solubility of the protective oxide scale in the fused salt film, and thin-film electrochemical measurements are generally conducted to follow the chemistry of the salt film during attack. The metal/scale interfacial studies seek to examine the role of interface dislocations in the creation/annihilation of point defects during scale growth, and the effect of segregated reactive elements on the kinetics of the interface reactions.

Applications, Engineering Achievements and Technology Transfer

Much of the research in the laboratory is accomplished with funding from the DOE Fossil Materials Program and EPRI Materials support. Accordingly, the research is aimed to solve problems related to coal-burning boilers, coal gasifiers, incinerators, utility gas turbines, and related industrial systems. The interfacial studies are conducted in collaboration with Pieraggi, B., Prof. in Toulouse, with NATO support for travel funds, and the research is quite fundamental and conceptual in nature. A patent has been recently granted for a pack cementation process to codeposit Cr and Si into steels; this technology has been licensed to Babcock and Wilcox for commercial implementation. Likewise, coatings for the formation of $Fe(Al,Cr)_3$ on steels, for $Mo(Si,Ge)_2$ for $Ti(SiGe)_2$ and SiC on carbon are likely to find future application. The advances made in explaining the reactive element effect in scale growth should find interest and extension quite generally in high temperature corrosion.

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Technical Key Words: Aerospace systems: Engine materials; Combustion systems: Fossil fuel-fired boiler; Waste incineration; Gas turbines: Aeroengines; Combustors; Land-based gas turbines; Oil and gas industries: Petrochemical industry; Others: Heat treating equipment; Industrial furnaces

SCOPE OF RESEARCH

Specific Topics

1. Static Oxidation Database

The program covers a wide range of commercial alloys including stainless steels, Fe-Ni-Cr alloys, and Ni- and Co-base superalloys. The objective is to define the capability of oxidation resistance in air for various commercial alloys, based on the oxidation damage in terms of metal wastage and internal penetration. Long-term oxidation behavior of alloys in air is also being investigated for exposure times up to one year with once-a-month cycle to room temperature for weighing of test samples. Attempts will be made to understand the breakaway oxidation for each alloy system and the influence of alloying elements.

2. Sulfidation Behavior of Alloys

Sulfidation resistance of commercial Fe-, Ni- and Co-base alloys is evaluated in 'reducing' atmospheres. The reducing environment consists of H_2-CO-CO_2-H_2S mixture. Tests are performed at temperatures ranging from 760 to 1090°C (1400-2000°F) for 200 to 1000 hours. Attempts will be made to understand breakaway corrosion and the influence of alloying elements.

3. Metal Dusting

The resistance to metal dusting for various alloys is investigated in H_2-CO and H_2-CO-CH_4 mixtures. Tests are conducted at 538-760°C (1000-1400°F). Correlation between alloy composition and materials resistance to metal dusting will be examined.

4. Chloride Effects in High Temperature Corrosion

The effect of chlorides on high temperature corrosion in a simulated combustion atmosphere (N_2-O_2-CO_2-SO_2 gas mixture) is investigated. The testing is conducted in a modified "Dean" Rig examining the corrosion attack by chloride vapor as well as chloride deposit. Different chlorides will be examined. The major objective is to understand better the corrosion reaction in many 'real' industrial environments which are frequently contaminated with chloride vapors and/or chloride deposits.

5. Fuel Ash Corrosion

Tests are conducted in a simulated combustion atmosphere (N_2-O_2-CO_2-SO_2-SO_3 gas mixture) with specimens imbedded in a synthetic fuel ash. The current program investigates coal ash corrosion using a synthetic ash mixture of Na_2SO_4-K_2SO_4-Fe_2O_3. The future program will investigate oil ash corrosion. Correlation between alloy composition and the corrosion resistance will be examined.

6. Field Corrosion Database

Field testing is being carried out in various operating plants. Coupon racks or individual coupons are exposed in actual operating environments, and then examined in an effort to determine the corrosion mode(s) as well as the relative alloy performance ranking.

7. Computerized High Temperature Corrosion Database

High temperature laboratory corrosion data and field tests data have been compiled in a computerized database. This system allows easy retrieval of data on a wide range of commercial alloys in a wide variety of corrosive environments.

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Scientific Key Words: Growth stress; Interface microstructure and microchemistry; Oxide fracture strain; Interfacial fracture resistance; Reactive element effects; Stress theoretical models

Technical Key Words: XRD stress determination; Acoustic emission; Strain measurements; Oxide fracture strain

SCOPE OF RESEARCH

Fundamental Approach

Oxide scales that protect alloys during exposure to high temperature oxidizing conditions invariably develop stresses, which sometimes can be large enough to cause the scale to fracture and spall. This research is concerned with the origins, magnitudes, progression with time and consequences of these stresses. Even though mechanical damage to scales is often the principal cause of failure in many high temperature applications, these stresses are not well understood, and consequently there is no general model for predicting their magnitudes or behavior with time. It appears at the moment that several factors, including details of the scale growth mechanism and the structure of the scale, can influence the stresses; therefore, experimental measurements are needed. The thrust of the work has two parts: (a) experimental measurements of stresses in the oxide and metal substrate, together with measurements of scale fracture, which have been applied to both model alloys and commercial alloys, and (b) the development of models to describe the stresses and scale fracture, with current emphasis on the evolution of stresses with time. The stress measurements are based primarily on in-situ X-ray diffraction, and scale fracture has been characterized with acoustic emission.

Applications, Engineering Achievements and Technology Transfer

By measuring strains in oxide scales at the growth temperature and during cooling, it has been shown that stress relaxation occurs during cooling, probably via metal creep at the higher temperatures and via scale spallation at lower temperatures. This means that ambient temperature strain measurements are not a reliable indicator of strains existing at the growth temperature. From measurements of both scale fracture and scale strains on similar alloys containing reactive elements (Ni-30Cr and Ni-30Cr-0.5Y), it has been possible to show that Cr_2O_3 scales on yttrium-containing alloys develop higher average stresses, but are significantly more resistant to cracking. While the incorporation of Y into the scale, or at the scale/metal interface, may make the scale inherently stronger, other factors, especially the typically convoluted metal/scale interface exhibited by the Y-containing alloys, are also likely to play an important role. A first attempt to infer fracture mechanics parameters, such as the distribution of flaw lengths, has been made from a statistical analysis of spallation combined with acoustic emission data. An expansion of the application of fracture mechanics concepts to scale fracture and spallation could lead to predictive capabilities useful for commercial applications.

It is proposed that the evolution of stresses during oxidation is determined by a dynamic balance between strain generation arising from the oxide growth processes and oxide/metal thermal expansion mismatch during cooling. Strain relaxation may occur via creep of the substrate or by scale cracking. The objective is to understand the progression of the stresses that develop in an oxide scale during high temperature oxidation and subsequent cooling. Several factors play important roles. The objective has several parts:

(a) Obtain experimental stress history data to evaluate the extent to which substrate creep or scale cracking is responsible for stress relaxation.

(b) Develop a computer model to account for the progression of scale stresses in terms of materials properties and scale growth mechanisms, considering especially stress generation during isothermal oxidation and stress relaxation by substrate creep. Input to this model will include experimentally measured stresses and gradients in the scale thickness direction, as well as thermal stresses due to oxide/metal thermal expansion mismatch.

(c) Characterize scale cracking at measured stresses and compare with that predicted by current theories.

This project is sponsored by the U.S. National Science Foundation.

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Scientific Key Words:	Aluminides; Bond/thermal barrier coatings; Ceramics degradation/interfaces/coatings; Mechanical behavior of scales; Multiphase alloys; Performance/lifetime; Reactive element effect
Technical Key Words:	Hot gas filtration; Integrated gasification combined cycle (IGCC); Newsletter; Pulp/paper boilers; Syngas coolers; Thermal barrier coating systems; Very high-temperature heat exchangers

SCOPE OF RESEARCH

Fundamental Approach

The scope of research on high-temperature corrosion and associated environmental effects at Oak Ridge National Laboratory (ORNL) is fairly broad. Over the period of January 1993 to September 1996, wide ranging studies of conventional and advanced alloys and coatings, ceramics, and ceramic-matrix composites in simple and complex high-temperature environments have been conducted. Despite this diverse mix of projects, there is a common theme underlying a number of these projects: the development of an understanding as to how to establish and maintain protective scales effectively. This is accomplished through the development of the relationships among material compositions, microstructures (of scales as well as the substrates on which they are grown), phase stabilities, reaction thermodynamics and kinetics, the mechanical integrity and adhesion of these surface products, and performance (as characterized by overall corrosion behavior and effects on properties). Such work then forms the basis for examination of corrosion resistance (or lack thereof when protective scale cannot form) and associated materials selection in aggressive or complex environments (multioxidant, molten salts, etc.). A key aspect of many of the studies is a focus on the ability to predict accurately material lifetimes in high-temperature corrosive environments. In numerous cases, this approach, which relies on a mechanistic understanding of the relevant corrosion phenomena as well as critical evaluation of appropriate experimental data, provides the necessary links between the basic scientific aspects of the ORNL studies and the applied or engineering nature of the other parts of the research efforts.

Applications, Engineering Achievements, and Technology Transfer

Almost all of ORNL's fundamental and applied efforts in high-temperature corrosion are sponsored directly or indirectly by the U. S. Department of Energy, with additional significant support from the Electric Power Research Institute. Consequently, much of the research is concerned with generic or targeted materials development associated with increases in efficiency and decreases in environmental impacts. Other work is targeted at specific improvements in components of energy-production systems or in end-use processes that are energy intensive. Specific systems and applications include coal combustion and gasification (low-NO_x combustion, effects of coal composition, hot-gas filtration), steam-reforming and ethylene cracking (gas handling), natural-gas- and indirectly-fired gas turbines (thermal barrier coatings, advanced heat exchangers), fusion reactors (first-wall and blanket systems), spallation neutron production systems, pulp and paper plants (recovery boilers, tube walls), and various components associated with high-temperature chemical processing. Many of the research projects in this area are conducted in formal or informal collaboration with industrial personnel associated with energy production and use, or with materials suppliers through cooperative research and development agreements, or interactions with industrial working groups or steering committees. Engineering achievements and technology transfer are often in the form of materials selection or lifetime prediction for specific materials and components in utility or industrial systems.

Specific Topics

1. Oxidation and Sulfidation of Iron-Aluminide Alloys and Coatings

Iron aluminides containing greater than about 20-25 at.% Al have oxidation/sulfidation resistance at temperatures well above those at which these alloys have adequate mechanical strength. In addition to alloying and processing modifications for improved creep resistance of wrought material, this strength limitation is being addressed by development of oxide-dispersion-strengthened (ODS) iron aluminides and by evaluation of Fe_3Al alloy compositions as coatings or claddings on higher-strength, less corrosion-resistant materials. As part of these efforts, which are supported by the Office of Fossil Energy of the U. S. Department of Energy, high-temperature corrosion studies of iron-aluminide weld overlays and cast and ODS Fe_3Al alloys are being conducted under isothermal and thermal cycling conditions in air, oxygen, and mixed gases containing H_2S or SO_2 (to simulate qualitatively environments associated with use of coal-derived fuels). The effects of reactive-element metal or oxide additions to Fe_3Al alloys on scaling and spallation have been evaluated. It was demonstrated that no other cation oxide dispersion performs better than Y_2O_3 in improving the high temperature oxidation resistance of iron aluminides and that excessive void formation at the metal-scale interface results in poor scale adhesion. Alloy compositions showing exceptional resistance in sulfur-bearing gases at 700-800°C have been identified.

2. Quantification of the Reactive Element Effect in ODS FeCrAl Alloys

A set of oxide-dispersion-strengthened (ODS) Fe-20 at.% Cr-10 Al alloys was produced with 30 different cations as oxide dispersions. Using cyclic and isothermal oxidation experiments at 1000°-1300°C and scanning and transmission electron microscopy characterization, the effect of each dopant on scale adhesion, alumina morphology, and oxidation kinetics was quantitatively described. Optimum doping levels are being estimated for the most effective dopants. Analytical electron microscopy studies of the external α-Al_2O_3 scale determined that the grain boundary segregation of cation dopants is not a sufficient criterion for a beneficial effect of the dopant on high-temperature oxidation performance. This work has corroborated the dynamic segregation model in explaining the reactive element effect on oxidation behavior.

3. Oxidation of Cast and Oxide-Dispersed β-NiAl

A detailed study, in collaboration with Hobbs, Linn, Prof., at MIT, is being conducted on the effect of oxygen active elements (Zr, Y, Hf, La and Ti) on the scale adhesion, oxidation kinetics, and alumina phase composition and morphology associated with β-NiAl. Cyclic and isothermal testing at 1000°-1300°C is being used to compare the effects of oxide dispersions to alloy additions. In general, the oxide-dispersed materials are less oxidation resistant than similar cast compositions, particularly for additions of Hf and Zr.

4. Mechanically Reliable Oxide Scales and Coatings

This is a multi-laboratory effort involving Lawrence Berkeley National Laboratory, Argonne National Laboratory, Lawrence Livermore National Laboratory, and Idaho National Engineering Laboratory in addition to ORNL, which has project coordination responsibility. The overall objective of the research is to generate systematically the knowledge required to establish a scientific basis for design and synthesis of improved (slow growing, adherent, sound) protective oxide coatings and scales on high-temperature materials without compromising the requisite bulk properties. The primary focus of the ORNL research is on the fundamental relationships among the microstructures of alumina scales or coatings, the oxide-metal interfaces, and the alloy substrates, the mechanical behavior of the surface oxides, and overall oxidation resistance. Use is made of scanning and transmission electron microscopy, nanoindentation, bend testing, gravimetric analysis, and positron spectroscopy. Comparisons of the characteristics of thermally grown scales to those of deposited alumina are used to understand better the various processes contributing to mechanical integrity and adherence of the surface oxides.

5. *High-Temperature Oxidation Behavior of Single Crystal Superalloys*

In support of the U.S. Department of Energy's Advanced Turbine Systems Program, scale spallation tendencies for Y-free, single-crystal, nickel-based superalloys processed in a commercial-scale desulfurization process by PCC Airfoils Inc. are being studied. In agreement with the results of Smialek, et al., NASA-Lewis, Cleveland, Ohio, desulfurization to less than approximately 0.4 ppm sulfur was required to match the cyclic oxidation behavior of a Y-containing version of the alloy. It was also shown that the Y-containing version of the alloy exhibited excellent resistance to scale spallation to 1150°C but that some spallation occurred at 1175°C, with massive scale loss at 1200°C. Complementary oxidation studies of other commercial single crystal alloys at 1000°-1200°C are also being conducted.

6. *Thermal Barrier Coatings on β-NiAl and Ni-Base Superalloys*

The adhesion of electron-beam, physical-vapor-deposited ZrO_2-Y_2O_3 coatings (produced by Nagaraj, B., at GE Aircraft Engines, Cincinnati, Ohio) and plasma-sprayed ZrO_2-Y_2O_3 coatings (produced by Brindley, W., at NASA-Lewis, Cleveland, Ohio) during thermal cycling in an oxidizing environment is being studied in support of the development of materials for high-efficiency, advanced land-based turbine systems. Characterization includes transmission electron microscopy of cross-sections of the oxide scale formed beneath the coatings. Substrate sulfur and yttrium contents have been shown to influence the lifetime of thermal barrier coatings on commercial Ni-base superalloys.

7. *Oxidation of Two-Phase Cr-Cr_2Nb/Cr_2Zr Alloys*

This project supports the development of high-strength, corrosion-resistant intermetallic alloys for use at very high temperatures in advanced fossil energy conversion systems. Alloy design approaches to the formation of protective scales on two-phase Cr-Cr_2Nb/Cr_2Zr alloys by compositional and microstructural control are being addressed. In addition, the coating of Cr-Nb (Zr) alloys for applications in sulfur-containing environments or at temperatures where chromia is no longer a stable solid phase is also being evaluated. Much of the work to date has concentrated on the Cr-Nb system, where it has been shown that oxidation resistance, in terms of reaction kinetics and scale adherence, increased with increasing volume fraction of the Cr-Cr_2Nb eutectic phase. The development of a multiproduct scale on hypoeutectic Cr-Cr_2Nb alloys and the dependence of oxidation behavior on niobium concentration are being evaluated in terms of applicable models for the oxidation of two-phase alloys.

8. Oxidation Lifetimes of Stainless Steel Foils

This work is being conducted in collaboration with Solar Turbines Inc., Allegheny-Ludlum, and the University of California at San Diego under the sponsorship of the Office of Fossil Energy, U. S. Department of Energy. Air oxidation of 75-150 μm thick foils of modified types 310 and 347 stainless steel is being conducted for up to 5000 h at 700° and 800°C. These data will be used to model the lifetime of the foils for application in recuperators. The effects of alloy additions of Ce, Zr, Si, Al and B on foil lifetime are being investigated

9. Oxidation and Oxidation/Corrosion of Niobium and Tantalum Alloys

Studies were conducted on niobium and tantalum alloys for space power applications. These alloys have excellent mechanical properties and corrosion resistance to liquid alkali metals at high temperatures, but they must be protected from oxidation to avoid deleterious effects on mechanical properties and corrosion resistance. Oxygen-uptake/oxidation rates of these alloys, Nb-1 Zr, PWC-11 and ASTAR-811C, were measured at oxygen partial pressures of 10^{-6} and 10^{-7} torr at temperatures up to 1080°C. For Nb-1 Zr and PWC-11, simultaneous oxidation/corrosion behavior in lithium was also determined.

10. Reactions of Hydrogen and Oxygen with V-Cr-Ti Alloys

Studies are being carried out to assess the effects of hydrogen and oxygen on the tensile properties of V-Cr-Ti alloys for fusion reactor blanket applications. Since the attractive mechanical properties of these alloys depend strongly upon the concentrations of interstitial elements, particularly oxygen and hydrogen, the aim of this work is to make a systematic study of the effect of pressure and temperature on oxygen and hydrogen uptake and to determine their effects on the tensile properties of V-5 Cr-5 Ti and V-4 Cr-4 Ti alloys. Individual and synergistic effects are being investigated as well as the mechanisms by which embrittlement occurs. Oxygen in these alloys greatly lowers the hydrogen content required for embrittlement.

11. Effects of Impurities in Coal on Fireside Corrosion in Boilers

This work is being conducted in collaboration with the Electric Power Research Institute and the Illinois Clean Coal Institute. The project is aimed at understanding and quantifying any role that chlorine in coal plays in the fireside corrosion of the waterwall and superheater regions of coal-fired boilers and involves several subcontractors. The approaches involve carefully-controlled tests in rigs designed to simulate the essential features of the regions of interest, using coals with selected levels or combinations of ash, sulfur, alkali metals, and chlorine. In-situ corrosion probes are being evaluated for use in operating boilers. These studies will culminate in a set of controlled corrosion tests in a full-scale boiler burning high-chlorine coals.

12. Assessment of Carbon Formation and Metal Dusting in Hot-Gas Cleanup Systems of Coal Gasifiers

The product gas resulting from the partial oxidation of carboniferous materials in a gasifier is typically characterized by high carbon and sulfur, but low oxygen, activity and, consequently, severe degradation of the structural and functional materials can occur. The objective of this task was to establish the potential risks of carbon deposition and metal dusting in advanced coal gasification processes by examining the current state of knowledge regarding these phenomena, making appropriate thermochemical calculations for representative coal gasifiers, and addressing possible mitigation methods and material selection guidelines.

13. Development of Materials for Black Liquor Recovery Boilers

Black liquor recover boilers are critical components in 80% of North American paper mills that use the kraft process. Almost all of these boilers utilize co-extruded 304L stainless steel/carbon steel tubing, but cracking in the stainless steel layer of these tubes has developed. This program is addressing this issue by characterizing the cracking that has been observed and the tube environment, determining the residual stresses in the tubes, conducting laboratory studies of stress-corrosion cracking and thermal fatigue, and then identifying alternate materials or processes. This work is being conducted in cooperation with the Pulp and Paper Research Institute of Canada and the Institute of Paper Science and Technology. An advisory group consists of representatives of 16 paper companies, 4 boiler manufacturers, and two tube fabricators.

14. High-Temperature Environmental Effects on Continuous Fiber-Reinforced Ceramic Composites

The purpose of this research is to determine the effects of representative high-temperature industrial environments on all properties that influence the effective lifetime of continuous fiber-reinforced ceramic composites. This is accomplished by developing an understanding of the environmental reactions in so far as they ultimately affect composite stability, damage tolerance, failure mode, etc. Gravimetric analysis is combined with scanning and transmission electron microscopy and mechanical testing to evaluate, for a given composite system and structure, the links between reaction kinetics, microstructural development, and the time dependence of properties changes. Particular emphasis is paid to the simultaneous influences of environmental reactions and stress. Because the overall program supported by this research aims at development of these ceramic composites for energy-efficient industrial applications, other work in this project examines the effects of exposures in simulated or actual application environments (for example, air-steam, air-SO_2, or H_2-CO).

15. High-Temperature Corrosion of Ceramic Heat-Exchanger Materials

This project provides technical support to a DOE-funded program with Stone & Webster Engineering Corporation. The purpose of the work is to assist in the selection of a ceramic material for use in an advanced high-temperature heat exchanger system. The original project addressed materials for a steam reformer while current studies are directed toward selecting materials for an ethylene cracker. Oxidation studies of various ceramic materials are being conducted at elevated temperatures and pressures in environments considered typical of these two process systems. These results will be combined with information collected from studies by Stone & Webster.

16. Newsletter on Materials and Components in Fossil Energy Applications

This Newsletter, sponsored jointly by the U.S. Department of Energy's Advanced Research and Technology Development Fossil Energy Materials Program and the Electric Power Research Institute, provides timely information concerning developments in, or performance results for, materials and components in conventional or new processes for the utilization of coal, or for the conversion of coal to other energy forms. The Newsletter has been published six times per year since 1975 and is available free of charge. An index, which is updated periodically, provides access to the information.

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SCOPE OF RESEARCH

1. *Oxidation of Structural Ceramics*

The oxidation behavior of structural ceramics is being studied at GE Corporate Research and Development in support of GE's aircraft engine and power generation businesses. Subjects of interest include the oxidation of Si-based ceramics in engine combustion environments including H_2O, CO and H_2, the effects of oxidation on the mechanical properties of fiber-reinforced ceramic composites, and methods to increase the oxidation resistance and service life span of ceramic components in aircraft engines and gas turbines.

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2. *Oxidation and Hot Corrosion of Metallic Components*

The oxidation and hot corrosion of metallic components is of interest to GE because of its aircraft engine and power generation businesses. Subjects of interest include oxidation of metallic superalloy coatings, coatings processes, simulation of turbine conditions in rig tests, and hot corrosion in alkali and vanadium containing environments.

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3. Thermal Barrier Coatings

The use of an insulating ceramic thermal barrier coating (TBC), typically a stabilized zirconium oxide, on the hot side of the metal to isolate the metal surfaces from direct contact with the hot gases is becoming critical to both the aircraft engine and power generation businesses. Topics in research and development of current interest include the following: understanding of processing/microstructure/property relationship, optimization of fabrication processes, understanding mechanisms of coating degradation and failure, coating characterization, and methodologies for life-prediction.

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Scientific Key Words:	High temperature water corrosion; Grain boundary structure; Creep/corrosion interactions; Nickel alloys; Cracking resistance
Technical Key Words:	Nuclear power systems; Steam generators; Surface engineering

SCOPE OF RESEARCH

Fundamental Approach

The focus of the research is on high temperature corrosion and stress corrosion cracking of austenitic alloys. The emphasis is on the relationship between microstructure and localized corrosion and/or cracking mechanisms. The environment of interest is high temperature (288-360°C) water, with varying oxygen and hydrogen concentrations, solution conductivity and pH. The research includes fundamental studies of crack initiation and propagation, creep and hydrogen effects in austenitic iron- and nickel-base alloys used in power generation systems. A portion of the program is also aimed at high temperature corrosion of ion beam modified metals and alloys.

This Laboratory was established to provide a facility to conduct stress corrosion cracking and hydrogen embrittlement tests in high temperature aqueous environments and, in particular, light water reactor environments. The laboratory contains five refreshed autoclave systems (titanium or stainless steel construction), two mounted in constant extension rate machines and two in constant load machines, two static autoclaves (titanium construction) and two CERT machines for ambient temperature testing. A mini-autoclave is also available for repassivation experiments. The laboratory also contains two full-featured corrosion measurement systems and two additional potentiostats. SCC testing in both PWR and BWR environments is possible.

Specific Topics

1. *Intergranular Stress Corrosion Cracking of Nickel-Base Alloys in High Temperature Water*

This work focuses on the mechanism of intergranular cracking of Ni-xCr-9Fe-C alloys where $5 \leq x \leq 30$ in high purity hydrogenated water at temperatures of ~360°C. There are several directions to this research. One portion is aimed at determining the roles of Cr in the corrosion and stress corrosion cracking process since it has been established that increasing alloy Cr content results in increasing resistance to IGSCC. A second part focuses on the role of C both in solution and in the form of grain boundary carbides. C has been found to be a potent strengthener and strongly retards creep and IG cracking at 360°C. Another effort is aimed at determining how grain boundary misorientation affects the IGSCC behavior and if samples can be engineered with preferred or controlled misorientations which resist cracking at high temperatures. Results have shown that by increasing the fraction of special or low angle grain boundaries by a factor of two the creep rate can be reduced by a factor of 10.

2. *Effect of High Temperature Water on Creep of Nickel-Base Alloys*

High temperature water is considerably more aggressive than an inert environment in the deformation behavior of nickel-base alloys. Increases in the creep rate by a factor of 5 have been found for Ni-Cr-Fe alloys tested in 360°C, high purity water vs. that in 360°C argon gas. The creep rate enhancement is believed to be affected by the hydrogen overpressure in the water. Experiments are being conducted to determine the role of hydrogen in the creep of Ni-Cr-Fe alloys and to assess the role of hydrogen in the dislocation mechanics in this alloys system.

3. *Irradiation Assisted Stress Corrosion Cracking of Controlled Purity 304 SS*

This program addresses the issue of irradiation-induced grain boundary chemistry and structure changes and how they may impact on IGSCC in high temperature (288°C) water containing controlled amounts of oxygen (2 ppm) and with a solution conductivity of ~0.5 μS/cm. Samples are pulled in CERT tests in high temperature water after undergoing proton irradiation at temperatures from 200 to 600°C and to doses from 0.1 to 3 dpa, resulting in redistribution of the major elements at the grain boundary, segregation of impurities and a radiation damaged microstructure in controlled-purity heats. Results of CERT tests are measured in terms of the number of cracks in the gage section and the elongation of the test sample. Results to date indicate that radiation-induced segregation, the presence of hard spinel particles in the microstructure and the formation of a high aspect ratio crevice are the key factors in determining the cracking susceptibility of these alloys.

4. *Repassivationof Fe-Cr-Ni Alloys*

This program is aimed at determining whether grain boundary segregation is responsible for the enhanced cracking susceptibility of irradiated alloys. Samples are loaded in tension in a high temperature, flowing water environment in a special autoclave and the corrosion current is monitored. After some time, an additional load is applied to the sample, and the instantaneous elongation causes the oxide film to rupture. The dissolution current is measured from the onset of the load as a function of time, first on a millisecond time scale and later on a second time scale. The rate at which the current decays is a measure of the repassivation characteristic of the alloy and can be influenced by the composition of the grain boundaries.

5. *Corrosion of Ion Beam Modified Metals and Alloys*

This effort is aimed at understanding the effect of ion implantation on the corrosion and oxidation behavior of metals and alloys. Ion beam surface modification is conducted in the Michigan Ion Beam Laboratory for Surface Modification and Analysis (MIBL) by either direct implantation, ion beam mixing or ion beam assisted deposition. Implants have been made on Fe-Cr alloys, nickel-base alloys and high strength iron-base alloys used for bearings. Results show that ion implantation can be extremely effective in specific instances where the changes in surface composition create a more corrosion resistant alloy or phase.

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Scientific Key Words: Artificial microstructure; Chemical vapor deposition; Coating/modifying surfaces; Corrosion fatigue; Creep/oxidation; Future gas turbine materials; High temperature properties; Hot stage; Materials joining; Mechanical testing; Metal/oxide interface; Metallic material; Microstructural analysis; Oxidation and reduction; Refractory metals; Surface modification; Surface treatments; Titanium alloys; Tungsten

Technical Key Words: Airframe materials; Engine materials; Very high temperature heat exchangers; Future gas turbine materials; Super capacitors

SCOPE OF RESEARCH

Fundamental Approach

1. The group has designed and artificially stabilized grain architectures for high temperature materials. It has developed a method that enables the stabilization of artificial grain structure to very high homologous temperatures in refractory metals and in other high temperature alloys, including oxides.

2. Controlled growth of oxide films for capacitors has been undertaken.

3. Titanium alloys have been coated with protective surface layers of Cr or Si_3N_4 to enable bonding of porcelain overcoats for dental crowns.

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INDEX OF SCIENTIFIC KEYWORDS

INDEX OF TECHNICAL KEYWORDS

INDEX OF RESEARCHER NAMES