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ABSTRACTS

Seventh Annual Conference
on
FOSSIL ENERGY MATERIALS

U.S. Department of Energy
Office of Fossil Energy
Advanced Research and Technology Development

and

ASM International

May 11-13, 1993
Oak Ridge, Tennessee

Fossil
Energy
Program

Conference Chairpersons

R. R. Judkins, Manager
Fossil Energy Program
Oak Ridge National Laboratory

N. C. Cole, Manager
Fossil Energy Materials Program
Oak Ridge National Laboratory

E. E. Hoffman, Manager
National Materials Program
Department of Energy
Oak Ridge Field Office

Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program

Welcome to the Seventh Annual Conference on Fossil Energy Materials.

The objective of the Fossil Energy AR&TD Materials Program is to conduct research and development on materials for fossil energy applications, focusing on the longer-term needs for materials with general applicability to the various fossil fuel technologies. Research is aimed at a better understanding of materials behavior in fossil energy environments and the development of new materials capable of substantial improvement in plant operations and reliability.

The scope of the AR&TD Materials Program addresses materials requirements for all fossil energy systems, including materials for coal processing, coal liquefaction, coal gasification, heat engines and heat recovery, combustion systems, and fuel cells. Work is in progress at national and government laboratories, universities, and industrial research facilities on ceramics and new alloys. A major feature of the Program is the transfer of the developed technologies to industry.

General Conference Information

Presentations

- All slide presentations will be held in the main lecture hall of the American Museum of Science and Energy.
- All poster presentations will be held in areas adjacent to the main lecture hall.

Registration

- Participants and guests may register for the conference beginning at 7:15 a.m. Tuesday and Wednesday mornings and 8:00 a.m. Thursday.
- Coffee and refreshments will be provided prior to the start of each morning's session and during breaks.

General

- A list of all conference attendees will be provided. Please check your mailing address for correctness to ensure receipt of any subsequent mailings.
- A message board and telephone will be provided for your convenience in the vicinity of the registration desk. Messages received by the Garden Plaza will be posted prior to breaks.
- The conference telephone number for receiving incoming messages is:

  (615) 576-0052

  There are pay phones located outside the lobby area for making outgoing calls.

  The Garden Plaza facsimile service number is:

  (615) 481-2474

PROGRAM SUMMARY

Tuesday, May 11

7:15 Registration Desk Opens
Refreshments and Coffee

8:00 Welcome and Introductory Remarks

8:15 Session IA - Ceramics

9:35 BREAK

11:10 Poster Presentations

12:10 LUNCH

1:05 Poster Presentations

2:05 Session IB - Ceramics

3:25 BREAK

4:15 Adjourn

6:00 *Visit Old City*
Dinner and Speaker

Wednesday, May 12

7:15 Registration Desk Opens
Refreshments and Coffee

8:00 Welcome and Introductory Remarks

Wednesday (Continued)

8:10 Session IIA - New Alloys: Intermetallics

9:30 BREAK

11:05 Poster Presentations

12:05 LUNCH

1:05 Poster Presentations

2:05 Session IIB - New Alloys: Intermetallics

3:25 BREAK

5:00 Adjourn

Thursday, May 14

8:00 Registration Desk Opens
Refreshments and Coffee

8:30 Welcome and Introductory Remarks

8:40 Session IIC - New Alloys: Advanced Austenitics

10:00 BREAK

12:15 Adjourn

FINAL PROGRAM
SEVENTH ANNUAL CONFERENCE ON FOSSIL ENERGY MATERIALS

Tuesday, May 11, 1993

SESSION I - CERAMICS

Session IA - Ceramics
R. R. Judkins, Chairperson

7:15 Registration Desk Opens

8:00 Welcome and Introductory Remarks

8:15 *Fabrication of Fiber-Reinforced Composites by Chemical Vapor Infiltration,* D. P. Stinton, Oak Ridge National Laboratory

8:55 *Modeling of Chemical Vapor Infiltration for Fabrication of Tubes*, T. L. Starr, Georgia Tech Research Institute

9:35 **BREAK**

9:50 *Improved Fiber Coatings for Controlling Interfacial Forces in SiC Matrix Composites*, R. A. Lowden, Oak Ridge National Laboratory

10:30 *Joining of SiC Ceramics and SiC/SiC Composites*, B. H. Rabin, Idaho National Engineering Laboratory

11:10 **POSTER PRESENTATIONS**

Synthesis and Processing of Complex Ceramic Oxides, L. R. Pederson, Pacific Northwest Laboratory

Ceramic Membranes for High Temperature Hydrogen Separation, D. E. Fain, Oak Ridge K-25 Site

Engineering Scale Development of the Vapor-Liquid-Solid (VLS) Process for the Production of Silicon Carbide Fibrils, W. E. Hollar, The Carborundum Company

Microwave Sintering of ZrO_2 *- 12 mol%* CeO_2, M. A. Janney, Oak Ridge National Laboratory

12:10 **LUNCH**

1:05 **POSTER PRESENTATIONS**

Development of Silicon Nitride Composites with Continuous Reinforcement, T. L. Starr, Georgia Tech Research Institute

Electrochemical Processes at Interfaces and Mixed Conductor Development, L. R. Pederson, Pacific Northwest Laboratory

Investigation of Properties and Performance of Ceramic Composite Components, L. S. Oleksuk, Virginia Polytechnic Institute and State University

Cryogenic Compaction of Nanosize Silicon Nitride Powders, S. G. Malghan, National Institute of Standards and Technology

Fabrication of Full Scale Fiber Reinforced Hot Gas Filters by Chemical Vapor Deposition, R. G. Smith, 3M Company

Session IB - Ceramics
M. A. Janney, Chairperson

2:05 *Development of Nondestructive Evaluation Methods and Prediction of Effects of Flaws on the Fracture Behavior of Structural Ceramics*, W. A. Ellingson, Argonne National Laboratory

2:45 *Thin Film Ceramic Catalyst Support Materials*, A. G. Sault, Sandia National Laboratories

3:25 **BREAK**

3:35 *Advanced Ceramic Materials and Electrochemical Processes at Interfaces,* L. R. Pederson, Pacific Northwest Laboratory

6:00 **VISIT OLD CITY - Dinner**
Speaker - W. D. Manly, Executive Vice President, Cabot Corp. (Ret)-"Technology Transfer-What Works, What Does Not"

FINAL PROGRAM

Wednesday, May 12, 1993

SESSION IIA - NEW ALLOYS: INTERMETALLICS

Session IIA - Intermetallics
N. C. Cole, Chairperson

7:15 Registration Desk Opens

8.00 Welcome and Introductory Remarks

8:10 *Development of Ductile Fe_3Al-Based Aluminides*, C. G. McKamey, Oak Ridge National Laboratory

8:50 *Tensile Properties of As-Cast Iron-Aluminide Alloys*, S. Viswanathan, Oak Ridge National Laboratory

9:30 **BREAK**

9:45 *Weldability of Iron Aluminides*, G. M. Goodwin, Oak Ridge National Laboratory

10:25 *Weldability of Polycrystalline Aluminides*, G. R. Edwards, Colorado School of Mines

11:05 **POSTER PRESENTATIONS**

Low-Aluminum Content Iron-Aluminum Alloys, V. K. Sikka, Oak Ridge National Laboratory

The Influence of Processing on Structure and Properties of Iron Aluminides, J. K. Wright, Idaho National Engineering Laboratory

Mechanical Properties of Iron-Aluminum Alloys, D. J. Alexander, Oak Ridge National Laboratory

Hydrogen Induced Embrittlement of Fe_3Al Alloy FA-129 Under Cyclic Loading, N. S. Stoloff, Rensselaer Polytechnic Institute

12:05 **LUNCH**

1:05 **POSTER PRESENTATIONS**

Aqueous Corrosion and Corrosion-Sensitive Embrittlement of Fe_3Al-Based and Lean-Aluminum Iron Aluminides, R. A. Buchanan, The University of Tennessee

Corrosion Performance of Iron Aluminides, K. Natesan, Argonne National Laboratory

Resistance to Aqueous Corrosion of Steels Protected by a Cr-Si Diffusion Coating, R. A. Rapp, The Ohio State University

Elastic Behavior of Iron and Nickel Aluminides, M. N. Srinivasan, Texas A&M University

Session IIB - Intermetallics
J. K. Wright, Chairperson

2:05 *Environmental Effects on Iron Aluminide*, J. H. DeVan, Oak Ridge National Laboratory

2:45 *Electro-Spark Deposited Coatings for Fossil Energy Environments*, R. N. Johnson, Westinghouse Hanford Company

3:25 **BREAK**

3:40 *Cr_2Nb Development*, C. T. Liu, Oak Ridge National Laboratory

4:20 *Effects of Alloying and Temperature on the High Temperature Oxidation of Cr-Cr_2Nb*, P. F. Tortorelli, Oak Ridge National Laboratory

5:00 **ADJOURN**

FINAL PROGRAM

Thursday, May 13, 1993

SESSION IIC - NEW ALLOYS: ADVANCED AUSTENITICS

Session IIC - Advanced Austenitics
R. W. Swindeman, Chairperson

8:00 Registration Desk Opens

8:30 Welcome and Introductory Remarks

8:40 *Investigation of Austenitic Alloys for Advanced Heat Recovery and Hot-Gas Cleanup Systems,* R. W. Swindeman, Oak Ridge National Laboratory

9:20 *Fabrication of Advanced Iron Aluminide-Clad 304 Austenitic Stainless Steel Tubing,* W. Mohn, Babcock & Wilcox

10:00 **BREAK**

10:15 *Comparative Evaluation of the Weldability of Modified 800H and Other Advanced Austenitic Stainless Steels,* C. D. Lundin, The University of Tennessee

10:55 *Corrosion Performance of Materials in Coal-Combustion Environments,* K. Natesan, Argonne National Laboratory

11:35 *Fireside Corrosion Test of Candidate Superheater Alloys, Coatings and Claddings,* S. Van Weele, Foster Wheeler Development Corporation

12:15 **ADJOURN**

CERAMICS

SESSION I

FABRICATION OF FIBER-REINFORCED COMPOSITES BY CHEMICAL VAPOR INFILTRATION

D. P. Stinton, J. C. McLaughlin, and B. Foster
Oak Ridge National Laboratory

K. Reifsnider, W. Stinchcomb, and K. Liao
Virginia Polytechnic Institute

Fiber-reinforced composites are being developed for applications such as combustors, burner tubes, heat exchangers, headers, hot-gas filters and even rotors for stationary gas turbine engines. A forced-flow, thermal-gradient chemical vapor infiltration (CVI) process has been developed to fabricate composites of thick-walled tubular geometry common to many of the above-mentioned components. In the present program, Nicalon® preforms of tubular geometry were fabricated with different fiber architectures (filament winding, 3D-braiding, cloth wrapping) to tailor the mechanical properties for specific requirements. Nondestructive evaluation has been performed and room temperature mechanical properties including axial stiffness and shear modulus have been measured. Computed tomography revealed that cloth-wrapped composites contained severe delaminations, that filament wound composites contained oriented porosity, and that braided composites contained large pores. The axial stiffness measured on the cloth wrapped composite was consistent with published results by DuPont. Also consistent with DuPont's results, the axial stiffness was found to decrease with increasing temperature.

MODELING OF CHEMICAL VAPOR INFILTRATION FOR FABRICATION OF TUBES

T. L. Starr and A. W. Smith
Georgia Tech Research Institute

We describe our recent efforts in modeling of chemical vapor infiltration (CVI) for tube shapes. Our model matches the forced flow/thermal gradient CVI system at Oak Ridge National Laboratory.

Control of the thermal gradient in the radial direction is critical for attaining rapid, complete densification. The ORNL reactor geometry includes radiant heating of the fiber preform and our CVI model had to be modified to properly include this contribution to the overall energy balance. With this modification the model-predicted temperatures match experimental measurements at the preform surface. The model shows how the effective thermal conductivity between the preform and the watercooled gas injector controls the temperature gradient within the preform and provides target values that lead to full densification.

IMPROVED FIBER COATINGS FOR CONTROLLING INTERFACIAL FORCES IN SiC MATRIX COMPOSITES

R. A. Lowden, K. L. More, and N. L. Vaughn
Oak Ridge National Laboratory

A graphitic carbon interface layer has been used to control the forces at the fiber-matrix interface in Nicalon® and Nextel™ fiber-reinforced silicon carbide matrix composites. However, carbon exhibits poor oxidation resistance, and thus even short-term exposure of unprotected composites to elevated temperature results in significant degradation of mechanical properties. The properties of the composites are degraded due to the oxidation and removal of the carbon interface coating. Longer exposures result in the oxidation of the fibers and matrix to form silica, which with time bonds the components together, and produces brittle behavior. Hence, interface coatings with improved oxidation resistance are being examined.

Much of the work on alternate interface coatings for silicon-based composite materials has focused on the development of glass formers, materials that upon oxidation produce a glass phase that can flow to seal the surface of the underlying substrate, hindering further attack. Silica functions well as a surface coating at temperatures > 1500 K, however, at lower temperatures, the rate of oxidation is reduced, and in addition, the SiO_2 glass does not flow, limiting its effectiveness. Other glass forming compounds have been studied, with boron being the most frequently utilized addition for temperatures around 1273 K. Boron forms a glass with a melting point of ≈ 725 K that can flow more readily at lower temperatures to seal the surface of the material to be protected.

Boron nitride and boron-doped carbon were examined as interface coatings for Nicalon® and Nextel™ reinforced SiC composites. Chemically vapor deposited BN exhibits good oxidation to 1573 K, beyond which attack becomes significant due to the volatilization of the boron oxide (B_2O_3) glass. Thus silicon-doped carbon and porous SiC interface layers were also explored for higher-temperature applications. The interlayers were deposited on fiber preforms, which were then densified with a SiC matrix employing the forced chemical vapor infiltration process. Room-temperature flexure strengths of as-fabricated composites, and specimens exposed in air at temperatures to 1673 K, were measured to assess the oxidation resistance of the interlayers. Composition and microstructure were characterized using electron microscopy. The results were compared to earlier results for composites with graphitic carbon fiber coatings.

Nicalon®, Nippon Carbon Company, Tokyo, Japan.
Nextel™, 3M Corporation, Minneapolis, MN

JOINING OF SiC CERAMICS AND SiC/SiC COMPOSITES

B. H. Rabin and G. A. Moore
Idaho National Engineering Laboratory

This project is developing techniques for joining SiC-based ceramics for use in fossil energy applications at temperatures exceeding 1000°C. In this paper, recent progress is described on the processing and characterization of ceramic-to-ceramic joints produced using reaction bonding silicon carbide (RBSC) interlayers. This method is attractive because processing is conducted at relatively low temperatures; the RBSC interlayer is compatible with SiC; and joined components can exhibit mechanical properties and environmental resistance comparable to the base ceramic. Since external pressure is not required during joint fabrication, the method is practical and can be applied to large parts or complex shapes. Processing steps include tape casting of SiC+C powder precursors, clamping the tape between the ceramic parts, providing a lump of Si adjacent to the joint, and heating to ~1450°C to allow molten Si to infiltrate the joint via capillary action.

Considerable effort has been devoted to optimizing the tape casting process used to fabricate thin, flexible green sheets of the SiC+C interlayer precursors. Control of the starting particle sizes and slurry formulation are critical to achieve defect-free tapes having the desired green density.

SiC-to-SiC joints have been produced using pressureless sintered α-SiC as a model material. Strengths measured in four-point bending were comparable to the strength of the α-SiC for testing temperatures from 25 to 1200°C, and failure was frequently seen to originate outside of the joint from larger defects present within the base ceramic. Recent results from fracture toughness testing will also be presented. Efforts to demonstrate tube-to-tube joining using localized induction heating will be described.

SYNTHESIS AND PROCESSING OF COMPLEX CERAMIC OXIDES

J. L. Bates, T. R. Armstrong, L. A. Chick, J. J. Kingsley
and L. R. Pederson,
Pacific Northwest Laboratory

PNL is investigating the sintering behavior of alkaline earth-substituted lanthanum and yttrium chromites in air, because these materials may be used for the current interconnect in solid oxide fuel cells (SOFC). Extensive commercialization of SOFC technology may require co-sintering of the interconnect in high $P(O_2)$ atmospheres with other ceramic components at temperatures as low as possible. During the past year, a chromite powder has been developed, using glycine-nitrate combustion synthesis methods, that has the lowest reported air-sintering temperature to date. To achieve this improved performance, careful control of the chromite composition is required as well as the use of highly reactive particles that are produced via the glycine-nitrate process.

Tape calendering capabilities are being developed to fabricate useful single and multilayer ceramic structures. The process differs from other tape fabrication methods in that no solvents are used. Oxide powders are mixed directly with a polymer and then formed into a thin film by a high shear process, which controls the tape film thickness. The unfired, green tapes are flexible and can be cut to size, laminated, corrugated, or otherwise formed before firing. Tape calendering can produce unsupported structures with a minimum thickness of 50 μm after firing. Calendered tapes as little as 1 μm in thickness can also be fabricated directly onto microporous or dense supports. The calendering process also allows structures with gradient porosity to be fabricated easily.

Choice of the complexant/fuel in the combustion synthesis of ceramic oxide powders was shown to strongly affect the phase purity, particle size distributions and surface areas of the product. These properties are important considerations when the ceramic powders are consolidated and sintered to their final shape. A variety of fuels were examined, including urea, carbohydrazide, guanidine nitrate, tetraformal trisazine, oxalic dihydrazide, and sucrose. Autoignition temperatures were lowest when strong complexes were formed between the metal cation and the fuel. When strong complexes were not formed, the fuel and metal nitrates were more likely to decompose separately, leading to lowered phase purity.

CERAMIC MEMBRANES FOR HIGH TEMPERATURE HYDROGEN SEPARATION

D. E. Fain and G. E. Roettger
Oak Ridge K-25 Site

The technology to fabricate ceramic membranes with pore radii less than 10 Å appears to be established. Membranes have been made with all the gas flow through pores less than 10 Å radius. Currently, a major problem hindering further development is an accurate measurement of pore radii below 10 Å. That measurement is needed to interpret and guide variations in the fabrication parameters. Experiments have been conducted to evaluate the pore size by measuring the flow rates of gases with different diameters. The gases that have been used are helium, carbon dioxide, and carbon tetrafluoride. Variations in surface flow and other transport modes for the different gases make it impossible to interpret the pore radius from measurements made only at room temperature. A new flow measurement system has been constructed to measure the flow of these gases at temperatures up to 275°C. Some special design features were used and the measurement system is functioning very well. Initial measurements indicate that appropriate interpretation of the data can lead to excellent determinations of pore radii less than 10 Å in addition to the determination of separation factors at elevated temperatures. The status of these measurements and their relation to our transport model will be discussed.

Developments have led to the use of a glass with the proper coefficient of thermal expansion to quickly and effectively seal the ends of membranes to allow for better sealing of the samples in test systems.

ENGINEERING SCALE DEVELOPMENT OF THE VAPOR-LIQUID-SOLID (VLS) PROCESS FOR THE PRODUCTION OF SILICON CARBIDE FIBRILS

W. E. Hollar and W. H. Mills*
The Carborundum Company
*BP Research

The Phase I portion of the development program has been completed. Under this program, the following milestones were achieved:

- successful transfer of the LANL process technology to Carborundum
- evaluation of key fibril synthesis scaleup parameters
- development of a computer model which simulates reactor performance
- development of a process gas recycle system
- evaluation of beneficiation processes for fibrils of various lengths

Significant results and conclusions from this program will be discussed.

VLS SiC fibrils will be used as a reinforcement in ceramic matrix composite (CMC) applications. The long length of the fibrils relative to standard SiC whisker materials could allow the fibrils to behave similarly to continuous fibers. This, combined with the excellent thermal and mechanical properties of the VLS SiC fibril, could lead to high temperature ceramic matrix composites based on the fibril. A manufacturing process for converting the fibrils into well-aligned, high volume fraction yarns will be required to achieve this goal. Fibril characteristics and potential process concepts for successful yarn forming will be discussed.

MICROWAVE SINTERING OF ZrO_2 -12 mol% CeO_2

M. A. Janney, M. L. Jackson, and H. D. Kimrey
Oak Ridge National Laboratory

Sintering of ZrO_2-12 mol% CeO_2 was accelerated by microwave processing at 2.45 GHz as compared with conventional firing. However, the size of the "microwave effect" was significantly smaller than that which was previously observed for microwave sintering of ZrO_2-8 mol% Y_2O_3. The difference in the effect that the microwave field had on the two zirconia systems is interpreted in terms of their ionic conductivities. A working hypothesis based on the present results and those of other researchers was formulated. It proposes that the magnitude of the microwave effect that will be observed for a material is related to the magnitude of the ionic conductivity of that material.

DEVELOPMENT OF SILICON NITRIDE COMPOSITES WITH CONTINUOUS REINFORCEMENT

T. L. Starr, D. L. Mohr and J. A. Hanigofsky
Georgia Tech Research Institute

Silicon nitride matrix composites are fabricated using the reaction sintering process by combining ceramic fiber with silicon powder and converting the silicon to nitride at high temperature in a nitrogen atmosphere. Critical factors in achieving good composite properties are effective impregnation of the multifilament tows, fiber stability during processing and fiber-matrix interface in the final composite.

We form tube shapes by passing the Nicalon® fiber tow through a slurry of silicon powder, winding the fiber onto a mandrel to form a unidirectional composite. As compared to the previous cloth lay-up method, this fabrication scheme produces better matrix distribution between individual filaments. Nicalon® fiber stability during processing is enhanced by CVD coating as-received fiber with layers of carbon and silicon carbide prior to slurry impregnation and winding. Flexure bar and C-ring testing produces non-brittle fracture but significant shear failure parallel to the fiber direction.

ELECTROCHEMICAL PROCESSES AT INTERFACES AND MIXED CONDUCTOR DEVELOPMENT

G. E. Youngblood, J. L. Bates, J. J. Kingsley,
L. R. Pederson, A. S. Rupaal, W. J. Weber and C. F. Windisch, Jr.
Pacific Northwest Laboratory

Rates of oxygen reduction at the cathode/electrolyte interface of an electrochemical cell that simulated an operating solid oxide fuel cell were assessed for a variety of cathode materials. Using complex impedance with an unbonded interface cell design and dc polarization methods, the relative contributions of charge transfer, oxygen dissociation and diffusional processes could be distinguished. This experimental approach yielded intrinsic electrocatalytic activities for cathode materials as a function of temperature and oxygen partial pressure, independent of interfacial morphology. Electrocatalytic activities for substituted lanthanum manganites and yttrium manganites varied considerably depending on composition, but all showed intrinsic activities substantially higher than platinum.

Ceramics that conduct both ions and electrons (mixed conductors) are technologically important materials, with applications as semipermeable membranes in gas separation, as electrodes in solid oxide fuel cells, and as electrocatalysts. Oxygen transport can occur under open circuit conditions in such materials, driven only by a gradient in the chemical potential of oxygen. An increase in the rate of charge transfer reactions and a reduction in polarization effects are among the advantages of the use of mixed conductors as electrode materials in solid oxide fuel cells. Predominantly ionically-conducting ceria-zirconia compositions were doped with multivalent rare earth oxides to introduce extrinsic electronic conductivity. Electronic conduction was further enhanced by partial reduction. Substituted lanthanum-iron-cobalt oxide perovskites are also being assessed, some of which exhibit oxygen ion conduction more than an order of magnitude higher than stabilized zirconia.

INVESTIGATION OF PROPERTIES AND PERFORMANCE OF CERAMIC COMPOSITE COMPONENTS

W. W. Stinchcomb, L. Oleksuk and K. Reifsnider
Virginia Polytechnic Institute and State University

The objectives of this program are to develop and validate a test system and test methodology for the mechanical characterization of ceramic composite tubes under multiaxial cyclic and quasi-static thermo-mechanical loading, to use that test system and methodology to test, evaluate, and characterize ceramic composite tubes and their long-term performance in coordination with Oak Ridge National Laboratory and other developers and manufacturers of such tubes, and to develop predictive models for damage tolerance and reliability of ceramic composite components. Progress to date has included the design, construction, and commissioning of a servohydraulic test system that can be used to apply such loading under computer control, the development of test methodology for such testing, the mechanical testing of carbon fiber/borosilicate glass, SiC/SiC, and oxide/oxide tubes at room and elevated temperatures, and the development and validation of a life prediction model (MRLife). Several important features of the testing procedures and the results are discussed. Gripping and alignment methods have been established, and depend on the material system and the nature of the mechanical grips used for tension/compression/torsion loading. Nondestructive testing of the tubes before and after testing has been used to identify details of the processing which influence the properties and performance, as well as to follow the degradation of the materials at elevated temperature and stress. One result of particular interest is the dependence of the axial stiffness of the SiC/SiC tubes on exposure temperature and time. The results of a preliminary investigation of that dependence will be discussed.

CRYOGENIC COMPACTION OF NANOSIZE SILICON NITRIDE POWDERS

W. Chen, A. Pechenik*, G. Piermarini
S. J. Dapkunas and S. G. Malghan
National Institute of Standards and Technology
*AFOSR, Bolling Air Force Base
Washington, DC

Recently there has been significant interest in fabricating ceramics from nanosize primary particles of 1 to 100 nm diameter. Reducing the particle size into the nanometer range offers a number of potential advantages for processing of ceramic materials. For example, if the process of grain growth is suppressed, nanograin ceramic materials with new and interesting properties can be fabricated from nanosize particles. Another exciting opportunity is the possibility of sintering nanosize particle compacts to full density at much lower temperatures than those needed for sintering of micron size particle compacts.

In our past research, we compacted nanosize silicon nitride particles at liquid nitrogen temperature using liquid nitrogen as a lubricant. The compaction was performed in a diamond anvil cell. This cryogenic compaction approach was very successful in producing densely-packed compacts of nanosize particles that sintered close to full density at a much lower temperature than that required for the conventional processing of silicon nitride. In addition, the ceramics exhibited transparency after sintering. This technique provides a novel approach to fabricate dense parts from nanosize powders. As a follow up to this research, we decided to study the cryogenic compaction process in more detail by designing and constructing a special apparatus for fabricating larger samples than the ones made in the diamond cell, which were only 0.2 mm in diameter. The novel equipment is capable of producing 3 mm disk-shaped samples under vacuum or in a variety of controlled atmospheres at temperatures in the range of 77 to 1000 K, and pressures up to 3 GPa. In addition, throughout the compaction procedure, continuous measurements of volume of the sample, applied force, and frictional force between the sample and the die walls are performed. This novel equipment is described in this paper along with a number of experimental studies on a variety of nanosize powders.

FABRICATION OF FULL SCALE FIBER REINFORCED HOT GAS FILTERS BY CHEMICAL VAPOR DEPOSITION

R. G. Smith, J. H. Eaton, D. D. Johnson and E. A. Richards
3M Company

The goal of the work described here has been to develop a hot gas candle filter for testing in a particulate loaded hot gas environment. A ceramic fiber reinforced, ceramic matrix composite approach has been followed to fabricate this new candle filter versus most existing monolithic ceramic filter designs. This fabrication route should provide a filter which is lighter, thinner, less sensitive to alkali attack, and less sensitive to thermal shock.

The first phase of the program involved fabricating sets of two inch diameter by four inch long substrates that filter surface samples could be quickly fabricated over and tested to determine filter characteristics. This avoided going through the entire candle filter fabrication process to test each filter sample. Perforated metal was used as the substrate. Filament wound and slurry coated filter surfaces were fabricated over these substrates. Chemical Vapor Deposition, CVD, coated Nextel™ 312 two inch diameter sleeving was then used as a test substrate for testing the best of the above filter surfaces. Filter bonding experiments were also run on these CVD coated four inch long substrate - filter combinations.

Testing of the four inch length samples in a TSI 8110 filter tester with 0.1 micron diameter sodium chloride particles showed pressure drops increasing from 5 to 30 mm H_2O over 20 minutes of loading at a flow rate of 3.2 cm/s. The filter efficiency reached 99.9% within 9 minutes. This compares with parallel tests on a four inch length of commercially available monolithic silicon carbide filter with pressure drops increasing from 20 to 65 mm H_2O over 20 minutes of loading at a flow rate of 3.1 cm/s while the filter efficiency reached 99.9% within 8 minutes.

The second phase of the program was to fabricate two full size, 60 mm diameter by about 1575 mm length, candle filters for testing at the Westinghouse Science and Technology Center in a particulate loaded hot gas environment. The testing of two full size filters will begin March 1, 1993, and be completed (final report) about May 1, 1993.

DEVELOPMENT OF NONDESTRUCTIVE EVALUATION METHODS AND PREDICTION OF EFFECTS OF FLAWS ON THE FRACTURE BEHAVIOR OF STRUCTURAL CERAMICS

W. A. Ellingson, J. P. Singh, D. L. Holloway, S. L. Dieckman,
D. Singh, E. A. Sivers, S. H. Sheen, and M. J. Wheeler
Argonne National Laboratory

Characterization of ceramic matrix composites by nondestructive evaluation (NDE) methods and an understanding of fracture behavior, together with correlation of fracture and NDE data, may provide insight into the prediction of component performance and the development of process technology. Work in this program has emphasized continuous-fiber ceramic matrix composites (CFCCs) with two dimensional (2-D) lay-ups composed of chemical-vapor-infiltrated (CVI) SiC/SiC materials, primarily those made of Nicalon® plain weave with 16 x 16 tows/in. However, one sample that was examined comprised a three-dimensional (3-D) SiC/SiC braid made by Techniweave. All studied samples were provided by Oak Ridge National Laboratory or Ceramic Composites Inc. and consisted of 100 layers/in. or ≈40-45 vol.% fibers. Specimens with cloth lay-up orientations of 0/30/60, 0/90, and 0/45 were examined by 3-D X-ray microtomography to characterize in-plane fiber orientations. Current information suggests that fiber misalignment affects mechanical properties differently for differing materials.

A near-term goal has been to establish detection capability for angular orientation. By using a new 1024 x 1024 x 14 bit detector, hinges from 3-D X-ray CT data with pixel sizes of <140 μm and a special 2-D fast-Fourier transform (FFT) image processing analysis, we have shown that fiber orientations can be measured to $\pm$2-1/2°. We have also begun to explore 3-D FFT analysis to establish detection of 3-D braid/weave fiber spacing. Another NDE method, multinuclear (^{1}H, ^{13}C, and ^{29}Si) NMR spectroscopy, is being studied to determine the chemical state of the fiber surface and its potential impact on fiber pullout. Surface chemistry of fibers and the chemistry of the interfacial regions in composites are included in the study. We are also conducting initial studies to investigate the bulk composition of the matrix materials (α, β, amorphous phase, silica, and oxynitride concentration) and the surface chemistry of Si_3N_4 and SiC fibers. The first ^{29}Si NMR experiments have focused on enhancing the signal from the surface by selectively reducing surface relaxation. A third NDE approach being explored is a low-frequency (0.5 MHz) acousto-ultrasonic method that measures time-of-flight of P-waves propagating in the composite. This method is being studied as a means to characterize, in a bulk sense, the fiber/matrix interfaces in CFCCs.

Fracture mechanics work to correlate with NDE data focused on strength distribution studies of as-fabricated Nicalon® fibers obtained from bundle tests. In addition, strength distribution of fractured Nicalon® fibers in composites was assessed by measuring fracture mirror radii. Scanning electron microscopy was conducted to determine the distribution of fiber pullout length distribution for fibers in composites, in order to accurately estimate their strength distribution. From the strength distribution plots, scale parameters were determined to be 3.45 GPa for as-fabricated fibers and 1.31 GPa for fibers in processed composites. However, the Weibull moduli for the two distributions were similar. The above-mentioned reduction in strength of the fibers in processed composites is believed to be due to surface flaws and defects, probably introduced during high-temperature processing and handling, as confirmed by a detailed fractographic evaluation.

Effects of fiber misorientation on mechanical properties of NDE-tested CVI continuous-fiber composites are currently being investigated in an effort to correlate NDE results (fiber orientation and density distribution) with fracture properties for continuous-fiber-reinforced ceramic matrix composites.

THIN FILM CERAMIC CATALYST SUPPORT MATERIALS

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and S. Srinivasan*
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*The University of New Mexico

Hydrous metal oxide materials (HMO) have shown great potential as ceramic catalyst supports due to a number of interesting properties. First, these materials contain large concentrations of alkali ions, imparting a high, intrinsic ion-exchange capacity which facilitates loading of transition metal cations. Through proper control of ion-exchange conditions high metal loadings can be achieved with essentially atomic dispersion of the metal. The unusual distribution of the transition metal cations on HMO supports after ion-exchange has important implications for the reduction of these cations to the metallic state. Results of studies of the reduction, activation, and catalytic activity of various metal cations supported on bulk hydrous titanium oxide (HTO) materials will be presented, with an emphasis on the differences between HTO supported catalysts and conventionally prepared titania supported catalysts. For metals such as nickel, which are relatively difficult to reduce, the high metal dispersion characteristic of the as-prepared catalysts is largely lost during reduction and activation. The catalytic behavior of Ni/HTO is therefore not significantly different from that of conventional Ni/TiO_2 catalysts. In contrast, easily reducible metals such as rhodium retain high dispersions during reduction, and the resulting catalytic behavior is substantially different from that of conventionally prepared Rh/TiO_2 catalysts.

A second useful property of HMO catalyst support materials is the ability to form thin films on a wide variety of substrates. This property raises the possibility of forming a thin, catalytic HMO film on another high surface area oxide, thereby allowing the catalytic and structural properties of the catalyst to be engineered independently. Two important challenges in the development of thin film HMO catalysts are the creation of porosity within the films, and the attainment of high coverage of the host support by the HMO film. For HTO films, we are addressing these challenges through variation of the properties of the sol-gel precursors used to form the HTO film. The film surface area resulting from various synthesis procedures can be measured using isopropanol dehydration, which occurs selectively on titania surfaces but not on potential host supports such as silica or alumina. Bulk HTO support materials with known surface areas provide calibration standards for this technique.

ADVANCED CERAMIC MATERIALS AND ELECTROCHEMICAL PROCESSES AT INTERFACES

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Pacific Northwest Laboratory

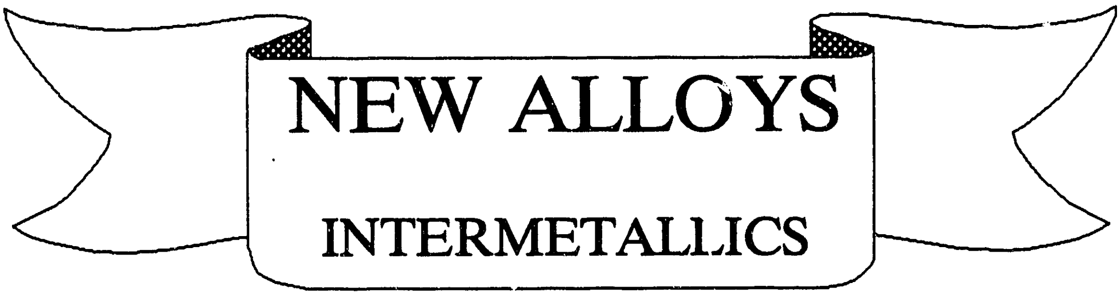
The purpose of this project is to identify new ceramic materials for use in fossil energy systems, to develop novel synthesis and processing methods for advanced ceramics, and to develop tools to follow the kinetics and mechanisms of electrochemical processes occurring at electrode/electrolyte interfaces.

Significant progress has been made in controlling the sintering of complex chromites, used as electrical interconnects in solid oxide fuel cells. Small changes in stoichiometry of these perovskites can be used to promote liquid-phase sintering and rapid densification. Temperatures required to sinter the complex chromites to full density have been lowered by several hundred degrees as a result.

Mixed electron- and ion-conducting ceramics consisting of ceria-zirconia doped with multivalent rare earth oxides were developed and characterized. Multivalent rare earth ions served to introduce extrinsic electronic conductivity into predominantly ionically-conducting solids. Thermodynamic parameters for oxygen vacancy formation in mixed oxides were obtained by thermogravimetry in oxygen-controlled environments. The mixed conductors are potentially useful as electrodes in electrochemical cells and as passive oxygen separation membranes.

Complex impedance and dc polarization methods were refined to allow fundamental steps in the reduction of oxygen at the cathode/electrolyte interface to be distinguished. Intrinsic electrocatalytic activities of electrode materials for oxygen reduction were obtained as a function of temperature and oxygen partial pressure, independent of interfacial morphology.

Tape calendering capabilities are being developed to fabricate multilayer ceramic structures. Oxide powders are mixed directly with a polymer and then formed into a thin film by a high shear process. The green structures are flexible and can be cut to size, laminated, corrugated, or otherwise formed before firing. Individual layers as little as 1 micron in thickness can be obtained by tape calendering.



NEW ALLOYS

INTERMETALLICS

SESSION IIA & IIB

DEVELOPMENT OF DUCTILE Fe_3Al-BASED ALUMINIDES

C. G. McKamey and V. K. Sikka
Oak Ridge National Laboratory

Iron aluminides based on Fe_3Al are of interest because of their excellent oxidation and corrosion resistance, especially in sulfur-bearing atmospheres. The work at Oak Ridge National Laboratory (ORNL) has centered on developing Fe_3Al-based alloys with improved ambient temperature ductilities and increased strengths at temperatures of 600-700°C. We now know that ambient temperature brittleness in this system is not inherent, but is caused by atomic hydrogen which is produced by an environmental reaction between aluminum in the alloy and water vapor in the atmosphere. We have made great strides in understanding this embrittling phenomenon and are now producing, through modifications in alloy composition and thermomechanical processing techniques, alloys with room temperature ductilities of >10% and tensile yield strengths at 600°C of as high as 500 MPa. Creep rupture lives over 200 h at 593°C (1100°F) and 207 MPa (30 ksi) can also be produced through control of alloy composition and microstructure. This presentation reviews past Fe_3Al development efforts and summarizes our present efforts to improve the tensile and creep rupture properties. The present status of our understanding of the role of composition, heat treatment, and microstructure on minimizing environmental embrittlement in this system will also be reviewed.

TENSILE PROPERTIES OF AS-CAST IRON-ALUMINIDE ALLOYS

S. Viswanathan, C. G. McKamey, P. J. Maziasz and V. K. Sikka
Oak Ridge National Laboratory

The understanding and control of cast structure is an important step in making iron-aluminide alloys viable engineering materials. This includes understanding the various components of cast structure, their evolution, their properties, their behavior during further processing, and finally their effect on mechanical properties. The first phase of this research characterized the various components of cast structure in FA-129 alloy. This phase of research characterizes the mechanical properties of Fe_3Al based alloys.

Room temperature tensile properties of as-cast Fe_3Al, Fe_3Al with chromium, and Fe_3Al based FA-129 alloy are investigated. Tensile properties are obtained in the as-cast condition, and after homogenization at 700, 900, and 1200°C. Transmission electron microscopy is used to characterize ordered phases and optical metallography and scanning electron microscopy are used to characterize the microstructure and fracture morphology. Tensile properties are correlated with microstructure and fracture morphology and some observations are made about tensile properties, in particular the ductility in the as-cast condition.

WELDABILITY OF IRON ALUMINIDES

G. M. Goodwin, C. J. McKamey, P. J. Maziasz and V. K. Sikka
Oak Ridge National Laboratory

Corrosion-resistant, weldable iron aluminide alloys with improved high-temperature strength are being developed for structural applications, and as weld overlay cladding for conventional structural steels and alloys. The effort is jointly funded by the Fossil Energy Materials Program and the Advanced Industrial Concepts Materials Program.

The iron-aluminide alloys are found to have highly variable susceptibility to weld hot cracking as a function of minor alloying additions over a wide range of aluminum content. In general, the higher aluminum content alloys are somewhat more resistant to hot cracking, and by careful choice of alloying additions, cracking resistance equivalent to commercial austenitic stainless steels can be achieved. Improved weldability, however, is usually at the expense of high-temperature strength.

Delayed cold cracking, presumed to be hydrogen-related, is also an important consideration in welding these alloys, either as monolithic materials, or as weld overlay cladding on stainless or low alloy steel substrates. We are employing various combinations of preheat and postweld stress relief heat treatments to assess the severity of this problem, and have determined that heat treatment in excess of 400°C following welding will be required to avoid delayed cracking.

Due to the difficulties encountered in fabricating some of the alloy compositions into wire or rod, we are also pursuing the formulation of coated electrodes for use in shielded metal arc (SMA) welding. Initial attempts have shown very high aluminum losses in the welding arc, and additional batches of electrodes are being formulated and produced.

WELDABILITY OF POLYCRYSTALLINE ALUMINIDES

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The cracking susceptibility of iron aluminide alloy FA-129 was evaluated using a sigmajig test apparatus. Samples of three base material microstructures (unrecrystallized and stress relieved, fine grain size (38μm) and coarse grain size (58μm)) and two welding speeds (30 ipm and 10 ipm) were tested in dry and moist (0.2-wt. pct. and 19-wt. pct. H_2O) atmospheres. The fusion zone grain size was observed to be insensitive to the base material grain size and the welding speed under these test conditions. The water vapor concentration present during welding was shown to have a dramatic effect on the fracture strength of the fusion zone, as expected. Fractures surfaces manifested brittle crack propagation, which was primarily confined to the fusion zone.

It was concluded that neither ordinary thermomechanical processing of base material to control grain size nor control of welding parameters to limit welding heat input were effective in preventing cracking in the presence of water vapor. Direct methods of refining the fusion zone grain structure during welding were suggested as potential means of improving the weldability in the presence of normal water vapor concentration.

LOW-ALUMINUM CONTENT IRON-ALUMINUM ALLOYS

V. K. Sikka, R. H. Baldwin and C. R. Howell
Oak Ridge National Laboratory

The low room-temperature ductility of Fe_3Al-based alloys is associated with their environment embrittlement. Reducing the aluminum level from 28 to 16 at.% has been found to be an effective method in essentially eliminating the environmental-embrittlement effect and increasing the room-temperature ductility value to over 25%. This poster will present data on alloy compositions, melting, casting and processing methods, and mechanical properties. Plans for future work on these alloys will also be described.

THE INFLUENCE OF PROCESSING ON STRUCTURE AND PROPERTIES OF IRON ALUMINIDES

J. K. Wright and R. N. Wright
Idaho National Engineering Laboratory

The effect of varying the amount of retained work during warm rolling and subsequent heat treatment on the development of microstructure in alloy FA-129 was examined in detail. The resulting property changes have been related to dissolution and reprecipitation of NbC, recovery of the defect structure, and the type and degree of order. A complex interaction between the defect substructure and the formation of DO_3 order during cooling from the B2 phase field was observed that has a significant effect on the tensile properties. Alloy FA-129 processed by inert gas atomization and hot extrusion was examined and found to have a uniform distribution of carbides that were significantly refined compared to cast material. There did appear to be a few large carbides remaining on grain boundaries.

Joining Fe_3Al using combustion synthesis from elemental powders was demonstrated. The microstructure in the joints has a fine grain size and the failure strength of joints is comparable to that of the base material. Failure occurs by debonding at the interface between the combustion synthesized Fe_3Al joint material and the base material. Correlation of microstructure and properties with processing variables will be presented.

MECHANICAL PROPERTIES OF IRON-ALUMINUM ALLOYS

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Oak Ridge National Laboratory

Tensile and impact tests have been conducted on specimens from a series of six heats of iron-aluminum alloys. These results have been compared to data for the iron aluminide alloy FA-129. The first of the new alloys was a simple ternary alloy of iron, aluminum, and chromium to match the FA-129 composition. The second was similar but with additions of zirconium and carbon. The third alloy had zirconium, carbon, niobium, and molybdenum. Three heats were produced with reduced aluminum contents so that a disordered body-centered cubic structure would be present. Additions of titanium or yttrium were included. The transition temperatures of all of the Fe_3Al alloys were similar, but the simple ternary alloy had a much higher upper-shelf energy. The reduced aluminum alloys had lower transition temperatures. The reduced aluminum alloy with the yttrium addition showed excellent tensile properties, and a very high upper-shelf energy level. Despite the high tensile ductility at room temperature, the transition temperature of the yttrium-containing alloy was still about 150°C, compared to approximately 300°C for FA-129. The impact properties, microstructures, and fractography of these alloys will be compared and discussed.

HYDROGEN INDUCED EMBRITTLEMENT OF Fe_3Al ALLOY FA-129 UNDER CYCLIC LOADING

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The effects of several gaseous environments and long range order on fatigue crack growth of Fe_3Al alloy FA-129 are described. The highest crack growth rates in both the DO_3 and B_2 conditions are observed for tests in hydrogen gas; lowest rates are achieved in dry oxygen or vacuum. Moist air produces intermediate growth rates. The results support the view that moisture in air causes hydrogen embrittlement under both monotonic and cyclic loading. However, the DO_3 condition is much more susceptible to the environment. When temperature is raised to 150°C, embrittlement is no longer observed. The fatigue crack results are supported by fractographic observations and transmission electron microscopy. A brief discussion of the mechanism of environmental embrittlement concludes the paper.

AQUEOUS CORROSION AND CORROSION-SENSITIVE EMBRITTLEMENT OF Fe_3Al-BASED AND LEAN-ALUMINUM IRON ALUMINIDES

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The University of Tennessee

Aqueous corrosion behaviors of Fe_3Al-based FAL-MO (Fe-28Al-5Cr-1Mo-0.04B-0.08Zr, at. %) were studied in 3.5 wt.% NaCl solution, under non-creviced and creviced conditions, and in thiosulfate and tetrathionate solutions over a range of concentrations. The FAL-Mo alloy was shown to have excellent resistance to pitting corrosion at room temperature in 3.5% NaCl, but the resistance decreased with increasing temperature, especially over the range 25-48C. Under creviced conditions, earlier work had shown the corrosion resistance of FAL-Mo to be comparable to that of 304L stainless steel in a mild acid-chloride solution (pH=4, 200 ppm Cl^-). In the present work, however, in the much-higher-chloride 3.5% NaCl solution, the crevice-corrosion resistance was shown to be somewhat less than that of 304L. In the sulfur-compound solutions, three iron aluminides were evaluated in 10^{-1}, 10^{-2}, and 10^{-3} M sodium thiosulfate and sodium tetrathionate. Only the FAL-Mo underwent passivation, with very low corrosion rates, and only at the two lower concentrations (10^{-2} and 10^{-3} M).

Aqueous corrosion behaviors and slow-strain-rate (SSR) ductilities of the new lean-aluminum iron aluminides were also studied (e.g., FAP-Y, Fe-16.1Al-5.4Cr-0.11C-O.11Zr-1.07Mo-0.959Y,at.%). In the mild acid-chloride solution, the pitting-corrosion resistances were comparable to that of the Fe_3Al-based FAL-Mo. In the higher-chloride 3.5 wt. % NaCl, the resistances were slightly less. Under SSR test conditions in the mild acid-chloride electrolyte, prior work had shown the ductilities (% elongations) of Fe_3Al based materials to be ~7% and ~1% at freely-corroding and hydrogen-charging potentials, respectively. Present studies on the lean-aluminum materials have shown the ductilities to be ~17% and ~5%, respectively. Thus, the present results indicate that these new materials have reasonably-good aqueous corrosion properties in chloride environments and significantly-enhanced ductilities under aqueous corrosion conditions.

CORROSION PERFORMANCE OF IRON ALUMINIDES

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Argonne National Laboratory

Iron aluminides are being developed for use as structural materials and/or cladding alloys in fossil energy systems. Extensive development has been in progress on Fe_3Al-based alloys to improve the engineering ductility of these alloys. This paper describes results from the ongoing program to evaluate the corrosion performance of these alloys. The experimental program at Argonne National Laboratory involves thermogravimetric analyses of alloys exposed to environments that simulate coal gasification and fluidized-bed combustion. Experiments were conducted at 650-1000°C in air, 1 vol.% CO-CO_2, and H_2-H_2S environments at two sulfur activities. In addition, oxidation/sulfidation behavior of several Fe-Al and Fe-Cr-Ni-Al alumina-forming alloys was determined for comparison with the corrosion rates obtained on iron aluminides. Other aspects of the program are corrosion evaluation of the aluminides in the presence of HCl-containing gases and in the presence of slag from a slagging gasifier. Upon completion of kinetic runs, the morphology and structure of the scales formed on the alloy surface were evaluated by scanning electron microscopy and X-ray analysis. Results are used to establish threshold Al levels in the alloys for development of protective alumina scales. Thermal cycling tests are used to examine the spalling resistance of the scales.

RESISTANCE TO AQUEOUS CORROSION OF STEELS PROTECTED BY A Cr-Si DIFFUSION COATING

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The simultaneous deposition of Cr and Si to form a diffusion coating on two steels (AISI 1045 and 4140) was studied. In halide-activated cementation packs, the use of either a "ternary activator" (e.g., $NaF+NaCl+AlF_3$) combined with the elemental metal powders, or else a "dual activator" (e.g., NaF + NACl) combined with a Cr-Si masteralloy powder, allows for the formation of a surface composition approximating 30Cr-3 to 4Si. Coated coupons were corrosion tested in either 1N H_2SO_4 or 3.5wt% NaCl solution at room temperature. Coupons coated using the Cr-Si masteralloy had superior corrosion resistance in 1N H_2SO_4, while steels coated in packs containing elemental metal powders suffered pitting corrosion. The coated coupons were not adequately resistant to pitting corrosion in 3.5wt% NaCl solution.

In accord with our previous experience, cementation packs using mixed chloride/fluoride activator salts resulted in extensive decarburization of low alloy steels, such that their properties following coating and heat treatment would not be satisfactory. Steels containing 5Cr were understandably not equally susceptible to decarburization. Thermodynamic stabilities for volatile compounds between carbon and the halogens indicate that the decarburization must result from the formation of carbon fluoride molecules. Therefore, further research was directed to achieve the desired Cr-Si codeposition without the use of fluoride salts. Recent progess is reported.

ELASTIC BEHAVIOR OF IRON AND NICKEL ALUMINIDES

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Texas A&M University

This paper summarizes the progress of research on understanding the elastic behavior of iron and nickel aluminides. The Young's modulus and the torsion modulus of the aluminides were determined using a Piezoelectric Ultrasonic Composite Oscillator Technique (PUCOT) setup. This consists of a drive crystal, a gage crystal, a spacer rod, and the specimen. The modulus values are determined by matching the frequencies of the drive crystal and the vibrational frequency of the specimen, while strain amplitude and damping are assessed when the gage crystal is added to the composite oscillation circuit.

The Young's modulus of Iron Aluminide: FAP-Y has been determined at room temperature, 300 and 600°C. The values are lowered very slightly with increase in temperature, indicating good tensile rigidity up to 600°C. Tests at 900°C are under way. Torsion modulus measured at room temperature indicates that the Poisson's ratio is about 0.19. Tests to determine the Poisson's ratio at higher temperatures are under way. The microstructure of FAP-Y shows well-developed equiaxed grains and therefore, lattice anisotropy seems to be the predominant factor for the relatively low Poisson's ratio of FAP-Y.

The results of tests carried out on powder-formed and cast NiAl will also be reported.

ENVIRONMENTAL EFFECTS ON IRON ALUMINIDE

J. H. DeVan and P. F. Tortorelli
Oak Ridge National Laboratory

The oxidation-sulfidation behavior of iron-aluminum alloys is being evaluated in high temperature mixed-oxidant atmospheres that arise in the combustion or gasification of coal. The alloys are of two general types: Fe_3Al-based alloys containing 28 atom % Al with variable additions of Cr, Nb, Mo, and Zr, and iron-aluminum alloys containing 16% Al, 5% Cr, 1% Mo, and 0.1% Zr (atom %). The corrosion evaluations are intended to establish the operating performance limits of the alloys, in terms of temperature and oxidant species (oxygen-sulfur-chlorine), at the respective aluminum concentrations, 16 and 28 atom %.

Based on weight changes in 1-4 week tests, air oxidation rates have been determined in isothermal tests up to 1300°C and in thermal cycling tests up to 1150°C. With the addition of 5% Cr, the oxidation resistance of the 16% Al alloy matches that of the 28% Al alloys (with or without Cr) at 900 to 1150°C. However, the higher level of aluminum is required to sustain oxidation resistance at temperatures above 1150°C, as determined in comparative isothermal tests at 1200 and 1300°C. Cyclic oxidation resistance of both the 16 and 28% Al alloys at 1000°C and above is significantly improved by the addition of 0.1% Zr. The addition of 0.1 and 0.5% yttrium to the 16%Al alloy gave no further improvement in oxide adherence compared to the 0.1% Zr addition alone.

Fe_3Al-based alloys have been supplied to the Coal Research Establishment of the British Coal Corporation for testing in a 0.5 tonne/h, pressurized, air blown gasifier located at Stoke Orchard. Corrosion results from two initial shakedown tests showed heavy pitting; however, this was attributed to downtime corrosion, which affected all of the lower chromium alloys under test. Testing is proceeding on a new set of Fe_3Al-based alloys together with the 16% Al alloy.

ELECTRO-SPARK DEPOSITED COATINGS FOR FOSSIL ENERGY ENVIRONMENTS

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Westinghouse Hanford Company

Electro-Spark Deposition (ESD) is a micro-welding process that uses short-duration, high-current electrical pulses to deposit or alloy an electrode material on a metallic substrate. The coating is fused (metallurgically bonded) to the substrate with such a low total heat input that the bulk substrate material remains at or near ambient temperature. Rapid solidification of the deposit typically results in an extremely fine-grained deposit that may be amorphous for some materials. Nearly any electrically conductive metal, alloy or cermet can be applied to metallic substrates.

The ESD process also allows multi-layer coatings to be built up using different materials to create graded structures or surface compositions that would be difficult to achieve by other means. A series of candidate Fe_3Al-based coatings were developed that involved multiple layers or ESD-applied alloying additions. The coatings were applied to type 316 SS and to Alloy 800 and include various combinations of Mo or Nb diffusion-barrier layers with Fe_3Al and Pd and Pt alloying additions. The coatings are in corrosion testing at ANL.

A new generation of iron aluminide coatings are now being developed using both Fe_3Al (as an intermediate layer) and FeAl to improve the corrosion performance of the surface by increasing the aluminum content. Earlier efforts resulted in inconsistent and defected coatings, but continued process parameter development (and the arrival of new electrode materials from ORNL) has now resulted in consistent, crack-free FeAl surface coatings.

Other advances include (1) the development of a new state-of-the-art power supply incorporating advanced computer interfacing and controls, and (2) successful new applications being developed commercially through technology transfer activities.

Cr_2Nb DEVELOPMENT

C. T. Liu
Oak Ridge National Laboratory

The objective of this task is to develop two-phase alloys based on Cr_2Nb and Cr(Nb) for structural use at high temperatures in hostile environments. The intermetallic phase Cr_2Nb is very hard but brittle at ambient temperatures. Current efforts on the development of Cr_2Nb/Cr(Nb) alloys are devoted to four areas: (1) preparation of high-purity materials with low levels of interstitial impurities, (2) control of relative amounts of Cr_2Nb and Cr(Nb) phases by adjusting niobium concentration, (3) control of microstructure by thermomechanical treatment, and (4) improvement in mechanical properties by alloying additions. The compressive ductility of the two-phase alloys can be increased steadily by reducing the amount of the Cr_2Nb phase. Room-temperature ductilities of >11% have been achieved by control of the Cr_2Nb phase and its precipitation reaction. The lowering in strength due to reduction in the Cr_2Nb amount can be compensated by alloying additions. New alloys developed at ORNL show a yield strength higher than 2000 MPa (300 ksi) at room temperature. Creep properties of the alloys at 1000°C are measured, and the results will be correlated with alloy composition and microstructure.

EFFECTS OF ALLOYING AND TEMPERATURE ON THE HIGH TEMPERATURE OXIDATION OF $Cr\text{-}Cr_2Nb$

P. F. Tortorelli and J. H. DeVan
Oak Ridge National Laboratory

As part of the effort to develop high-strength $Cr\text{-}Cr_2Nb$ alloys, experiments are being conducted to evaluate the most appropriate alloying and coating approaches to achieving good high temperature corrosion resistance. A study of the oxidation of representative $Cr\text{-}Cr_2Nb$ alloys as a function of temperature was initiated to quantitatively define the upper limit for effective protection by thermally grown scales. The baseline binary alloy containing 12 at.% Nb was oxidized in dry air at 900, 1000, and 1100°C using a microbalance. Results at 900 and 1000°C were consistent with previously reported data at 900 and 950°C in terms of the rates of weight gain and the general parabolic shapes of the kinetic curves. Exposure at 1100°C resulted in much worse oxidation behavior - a higher weight gain and a transition to a much higher oxidation rate after about 100 h were observed.

Results from the study of the isothermal oxidation of the binary Cr-Nb alloys indicated that increasing the volume fraction of the eutectic phase at the expense of the Cr-rich region by using niobium concentrations of at least 12 at. % appears to reduce scaling and spallation. It was therefore appropriate to examine the effects of macro- and microalloying on the oxidation resistance of $Cr\text{-}Cr_2Nb$ alloys containing 12 at.% Nb. The results revealed no dramatic effects of selected alloying additions on the rate of scaling.

NEW ALLOYS
ADVANCED AUSTENITICS

SESSION IIC

INVESTIGATION OF AUSTENITIC ALLOYS FOR ADVANCED HEAT RECOVERY AND HOT-GAS CLEANUP SYSTEMS

R. W. Swindeman
Oak Ridge National Laboratory

Commercial and developmental alloys were evaluated in support of advanced steam cycle and combined cycle technology. Working with industrial groups, grade 91 steel, which is a candidate for main steam line piping and superheater tubing in advanced steam cycle plants, was re-evaluated to examine metallurgical factors that influence long-time performance to 600°C. Deformation models and aging effect models were developed. The behavior of aluminum-bearing alloys and high chromium alloys was examined for potential applications to 870°C. Thermal cycling of clad tubing was undertaken, and good performance was found. Testing of corrosion-resistant filler metals for tubing was extended to times approaching 30,000 h. Good strengths were observed. Modified type 310 stainless steels were examined to 927°C. It was found that these steels had up to twice the strength of standard type 310H stainless steel.

FABRICATION OF ADVANCED IRON ALUMINIDE-CLAD 304 AUSTENITIC STAINLESS STEEL TUBING

W. R. Mohn and M. J. Topolski
Babcock & Wilcox Company

Selected compositions of iron aluminides based on Fe_3Al have been developed at Oak Ridge National Laboratory which exhibit excellent resistance to oxidation and sulfidation at high temperatures in corrosive environments. Effective implementation of these low cost materials to extend the useful lifetimes of critical superheater and reheater components could significantly improve the performance of fossil fueled energy generation systems. In a continuing project, funded by ORNL through the Fossil Energy Materials Program, researchers at the Babcock & Wilcox Research and Development Division have been investigating methods to produce duplex structural tubing consisting of iron aluminide-clad austenitic stainless steel for practical use in fossil fueled energy equipment. These efforts have resulted in the development of a processing sequence utilizing commercial metalworking practices to successfully fabricate iron aluminide-clad 304 austenitic stainless steel tubing. In this work, two hybrid hollow core billets were initially prepared (through hot isostatic pressing) and extruded in separate trials at 2200 and 2000°F. Both extrusions yielded 2-inch O.D. clad tubes, each approximately 18 feet long. Wall thickness was typically 0.375-inch, including a nominal clad layer thickness of 0.100 inch. The tubes were carefully examined and analyzed to characterize the bonding between the Fe_3Al clad layer and the 304 stainless steel substrate.

COMPARATIVE EVALUATIONS OF THE WELDABILITY OF MODIFIED 800H AND OTHER ADVANCED AUSTENITIC STAINLESS STEELS

C. D. Lundin and C.Y.P. Qiao
The University of Tennessee

The weldability of modified 800H was evaluated in terms of hot cracking susceptibility. Two other commercial alloys, HR3C and NF709, were employed to carry out a comparative study. Two tubing heats and eleven small laboratory heats of modified 800H, two commercial tubing heats of HR3C and one commercial tubing heat of NF709 were involved in this investigation.

It is found that modified 800H exhibits a good weldability in terms of operability with a better performance in terms of weld bead shape as contrasted to NF709. However, a higher hot cracking susceptibility for modified 800H tubing heats was found compared to HR3C and NF709. The results from the hot cracking evaluations on small laboratory heats of modified 800H indicated that modified 800H can have an equivalent hot cracking resistance compared to HR3C and NF709 if the grain size is properly controlled and an optimum thermal mechanical treatment is carried out.

A HAZ liquation cracking mechanism common to fully austenitic stainless steels and high nickel alloys is proposed and was used to interpret the hot cracking behaviors of the materials studied in this investigation. Additionally, the preliminary assessment results of HAZ softening behavior in modified 800H, HR3C, and NF709 are discussed.

CORROSION PERFORMANCE OF MATERIALS IN COAL-COMBUSTION ENVIRONMENTS

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Reliability of components and long-term trouble-free performance of structural materials are essential for the acceptance of power-generating processes that utilize coal as a feedstock. The combustion environments encompass a wide range of oxygen partial pressures, from excess-air conditions in conventional systems to air-deficient conditions in low-NO_x systems. Apart from the environmental aspects of the effluent from coal combustion, one of the concerns from the systems standpoint is the aggressiveness of the combustion environment toward the boiler structural components such as waterwall tubes and steam superheaters. The corrosion tests in this program address the combined effect of sulfur and chlorine on the corrosion response of several ASME-coded and noncoded boiler materials exposed to air-deficient and excess-air combustion conditions. Thermodynamic calculations were made to evaluate the gas chemistries that will arise from combustion of coals. The results of such calculations, coupled with oxygen-sulfur-chlorine thermochemical diagrams, are used to select gas environments for the laboratory test program. Tests were conducted at 400 and 650°C to simulate the waterwall and superheater environments, respectively, in pulverized-coal-fired boilers. Experimental results obtained thus far indicate that both sulfur and chlorine can accelerate corrosion of ferritic and austenitic alloys; further, the protective capacity of the oxide scale in resisting further corrosion seems to degrade in the presence of both sulfur and chlorine.

FIRESIDE CORROSION TEST OF CANDIDATE SUPERHEATER ALLOYS, COATINGS AND CLADDINGS

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Fireside corrosion, caused by liquid alkali-iron trisulfates (AIT), has been an obstacle to higher steam temperatures and to efficient utilization of high sulfur coals. Tests simulating the environment in the superheater bank of a pulverized coal-fired boiler were conducted on several promising new alloys and claddings. Alloys were exposed to a variety of synthetic ash and simulated flue gas compositions at 650 and 700°C for times ranging up to 800 hours. Included in the testing program were new high-chromium/high-nickel alloys, modified commercial alloys, lean stainless steels (modified type 316) clad with high-chromium/high-nickel alloys, and intermetallic aluminides.

Thickness loss measurements indicated that resistance to attack improved with increasing chromium level. Silicon and aluminum were also helpful in resisting attack, while molybdenum was detrimental to the resistance of the alloys to attack. Three different attack modes were observed on the alloys tested. Alloys with low resistance to attack exhibited uniform wastage, while pitting was observed in more resistant alloys. In addition to surface fluxing by molten alkali-iron trisulfates, subsurface sulfur penetration and intergranular attack also occurred.

While there is no complete solution to AIT attack, incremental improvements are being made. Alloys and claddings with a chromium content above 30 percent appear to have substantial resistance to attack, validating previous research. A new alloy, CR35A, and claddings of 690 and 671 had excellent resistance to attack.

The aluminide alloys tested showed wide variance in their resistance to both molten trisulfate attack and gas-phase attack. Neither the nickel aluminide nor the iron aluminide containing 2-percent chromium held up as well as the more conventional stainless steels. The iron aluminide containing 5-percent chromium performed as well as alloy 347. Given the low chromium content of the iron aluminides and their newness, further development of this alloy system may lead to alloys with improved molten trisulfate attack resistance.

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