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

FOSSIL ENERGY MATERIALS PROGRAM

**Semiannual Progress Report for the
Period Ending September 30, 1988**

Fossil Energy Materials Program Office

Oak Ridge National Laboratory
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for the U.S. Department of Energy

Fossil
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AR&TD FOSSIL ENERGY MATERIALS PROGRAM
SEMIANNUAL PROGRESS REPORT FOR THE PERIOD
ENDING SEPTEMBER 30, 1988

R. R. Jenkins, Manager
Fossil Energy Program

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PREVIOUS REPORTS IN THIS SERIES

- ORNL/FMP-81/1 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending December 31, 1980.
- ORNL/FMP-81/2 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending March 31, 1981.
- ORNL/FMP-81/3 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending June 30, 1981.
- ORNL/FMP-81/4 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending September 30, 1981.
- ORNL/FMP-82/1 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending December 31, 1981.
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ORNL/FMP-86/4 AR&TD Fossil Energy Materials Program Quarterly Progress Report for Period Ending September 30, 1986.

ORNL/FMP-87/1 AR&TD Fossil Energy Materials Program Semiannual Progress Report for Period Ending March 31, 1987.

ORNL/FMP-87/2 AR&TD Fossil Energy Materials Program Semiannual Progress Report for Period Ending September 30, 1987.

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PART I - INTRODUCTION

INTRODUCTION

R. R. Judkins and P. T. Carlson

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

The objective of the AR&TD Fossil Energy Materials Program is to conduct research and development on materials for fossil energy applications with a focus on the longer-term and generic needs of the various fossil fuel technologies. The program includes research aimed toward a better understanding of materials behavior in fossil energy environments and the development of new materials capable of substantial enhancement of plant operations and reliability.

The management of the Program has been decentralized to the DOE Oak Ridge Operations Office (ORO) and the Oak Ridge National Laboratory (ORNL) as technical support contractor. The organizational relationships among DOE Headquarters, ORO, and ORNL are illustrated in Fig. 1. A substantial portion of the work on the AR&TD Fossil Energy Materials Program is performed by participating subcontractor organizations. All subcontractor work is technically monitored by Program staff members at ORNL and Argonne National Laboratory (ANL). The performing institution, principal investigator, and technical monitor for each project are shown in Table 1.

The ORNL Fossil Energy Materials Program Office compiles and issues this combined semiannual progress report from camera-ready copies submitted by each of the participating subcontractor organizations. This report of activities on the program is organized in accordance with a work breakdown structure in which projects are organized according to materials research thrust areas. These areas are (1) Structural Ceramics, (2) Alloy Development and Mechanical Properties, (3) Corrosion and Erosion of Alloys, and (4) Assessments and Technology Transfer. A schematic summary of this organization is provided in Fig. 2.

ORNL-DWG 86-8234AR

Fig. 1. Organizational relationships among DOE-HQ, DOE-ORO, and ORNL for the AR&TD Fossil Energy Materials Program.

Table 1. Projects of the AR&TD Fossil Energy Materials Program

Project Work Breakdown Structure Element and Title	Performing Institution	Principal Investigator	Technical Monitor
Structural Ceramics			
AML-1(A), Development of Nondestructive Evaluation Methods for Structural Ceramics	Argonne National Laboratory	W. A. Kilgus	D. R. Johnson
AML-1(B), Effects of Flaws on the Fracture Behavior of Structural Ceramics	Argonne National Laboratory	J. P. Singh	P. R. Johnson
CT-1, Development of Advanced Fiber-Reinforced Ceramics	Georgia Institute of Technology	T. L. Starr	D. R. Johnson
CT-1(A), Modeling of Fibers Performed for CVD Infiltration	Georgia Institute of Technology	T. L. Starr	U. R. Johnson
ML-1(A), Nondestructive Evaluation of Advanced Ceramic Composite Materials	Idaho National Engineering Laboratory	J. B. Carter	D. R. Johnson
ML-1(B), Nondestructive Evaluation of Carbon-Carbon Composite Materials	Idaho National Engineering Laboratory	R. M. Rabin	D. R. Johnson
ML-1(C), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by Chemical Etching	Idaho National Engineering Laboratory	R. M. Neilson	D. R. Johnson
ML-1(D), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by X-Ray Diffraction	Idaho National Engineering Laboratory	P. D. Shukla	D. R. Johnson
ML-1(E), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by Ultrasonic Methods	Idaho National Engineering Laboratory	E. M. Peller	D. R. Johnson
ML-1(F), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by Infrared Spectroscopy	Idaho National Engineering Laboratory	D. P. Stinton	T. M. Rossmann
ML-1(G), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by Raman Spectroscopy	Idaho National Engineering Laboratory	R. A. Lunden	T. M. Rossmann
ML-1(H), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by Acoustic Emission	Idaho National Engineering Laboratory	M. E. Kile	M. R. Snyder
ML-1(I), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by X-Ray Fluorescence	Idaho National Engineering Laboratory	J. L. Bates	D. R. Johnson
ML-1(J), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by X-Ray Photoelectron Spectroscopy	Idaho National Engineering Laboratory	J. V. Bates	D. R. Johnson
ML-1(K), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by X-Ray Computed Tomography	Idaho National Engineering Laboratory	D. M. Dougherty	D. R. Johnson
ML-1(L), Nondestructive Evaluation of Fiber-Ceramic Matrix Composites by X-Ray Diffraction	Idaho National Engineering Laboratory	E. L. Reiffender	D. R. Johnson
Alloy Development and Mechanical Properties			
ML-2, Evaluation of the Fabricability of Advanced Austenitic Tubing	Rohm and Haas	E. E. Lebeau	R. V. Seidenman
ML-2, Investigation of the Weldability of Austenitic Aluminides	Colorado School of Mines	G. R. Edwards	R. R. Jenkins
ML-2, Mechanical Properties and Microstructural Stability of Advanced Austenitic Alloys	Cornell University	Chao-Yu Li	R. V. Seidenman
ML-2, Consolidation of Rapidly Solidified Aluminide Metal Powders	Idaho National Engineering Laboratory	J. E. Flinn	R. R. Jenkins
ML-2, Development and Evaluation of Advanced Austenitic Alloys	Idaho National Engineering Laboratory	R. V. Seidenman	R. R. Jenkins
ML-2, Fabrication Development of Nickel-Iron Aluminides	Idaho National Engineering Laboratory	V. R. Stiles	R. R. Jenkins
ML-2, Development of Iron Aluminides	Idaho National Engineering Laboratory	C. G. McManis	R. R. Jenkins
ML-2, Fundamental Study of Aluminizing and Chromizing Processes	Idaho National Engineering Laboratory	R. A. Rupp	J. R. DeVine
ML-2, Development of a Design Methodology for High-Temperature Cyclic Application of Materials Which Experience Cyclic Softening	Idaho National Engineering Laboratory	D. L. Harriott	R. V. Seidenman
ML-2, Microstructural Studies of Advanced Austenitic Steels	Idaho National Engineering Laboratory	J. A. Todd	R. V. Seidenman
ML-2, Investigation of Welding and Joining Techniques for Advanced Austenitic Alloys	Idaho National Engineering Laboratory	C. D. Lenden	R. V. Seidenman
ML-2, Investigation of Electro-Spark Deposited Coatings for Protection of Austenitic Alloys	Idaho National Engineering Laboratory	R. R. Johnson	R. R. Jenkins

Table 1. (continued)

Project Work Breakdown Structure Element and Title	Performing Institution	Principal Investigator	Technical Monitor
Corrosion and Erosion of Alloys			
ANL-3(A), Corrosion and Mechanical Properties of Alloys in PBC and Mixed-Gas Environments	Argonne National Laboratory	K. Matsen	J. H. DeVan
ANL-3(B), Surface Modification for Erosion/Corrosion	Argonne National Laboratory	G. R. Peneke	J. H. DeVan
BCL-3, Investigation of the Effects of Microalloy Constituents, Surface Treatment, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales	Battelle-Columbus Laboratories	I. G. Wright	J. H. DeVan
CWR-3, Investigation of the Effects of Microalloy Constituents, Surface Treatment, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales	Case Western Reserve University	K. H. Vedula	J. H. DeVan
LBL-3, Studies of Materials Erosion in Coal Conversion and Utilization Systems	Lawrence Berkeley Laboratory	A. V. Levy	R. R. Judkins
NIST-3, Mechanisms of Galling and Abrasive Wear	National Institute of Standards and Technology	L. H. Ives	R. R. Judkins
ORNL-3(A), Development of Surface Treatments and Alloy Modifications for Corrosion-Resistant Oxide Scales	Oak Ridge National Laboratory	J. H. DeVan	R. R. Judkins
ORNL-3(B), In-Situ Scanning Electron Microscopy Studies of Erosion and Erosion-Corrosion	Oak Ridge National Laboratory	J. R. Keiser	R. R. Judkins
PIT-3, Corrosion Mechanism of Coal Combustion Products on Alloys and Coatings	University of Pittsburgh	G. H. Meier	J. H. DeVan
UCB-3, Solid Particle Erosion in Turbulent Flows Past Tube Banks	University of California - Berkeley	J. A. C. Humphrey	R. R. Judkins
UCIN-3, Study of Particle Rebound Characteristics and Material Erosion at High Temperatures	University of Cincinnati	W. Tabakoff	R. R. Judkins
UES-3, Investigation of the Effects of Microalloy Constituents, Surface Treatments, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales	Universal Energy Systems	V. Srinivasan	J. H. DeVan
UND-3, A Study of Erosive Particle Rebound Parameters	University of Notre Dame	T. H. Kosel	R. R. Judkins
UTN-3, Aqueous Corrosion of Iron Aluminides	University of Tennessee	R. A. Buchanan	J. H. DeVan
VPI-3, Alkali Attack of Coal Gasifier Refractory Linings	Virginia Polytechnic Institute	J. J. Brown, Jr.	R. R. Judkins
Assessments and Technology Transfer			
B&W-4, Potential Applications of Structural Ceramic Composites in Gas Turbines	Babcock & Wilcox	W. P. Parks	D. R. Johnson
BCL-4, "Materials and Components in Fossil Energy Applications" Newsletter	Battelle-Columbus Laboratories	I. G. Wright	R. R. Judkins
ORNL-4(B), Coal Conversion and Utilization Plant Support Services	Oak Ridge National Laboratory	J. R. Keiser	J. H. DeVan

Fig. 2. Work Breakdown Structure for the AR&TD Fossil Energy Materials Program.

It is hoped that this series of AR&TD Fossil Energy Materials Program semiannual progress reports will aid in the dissemination of information developed on the program. Highlights of projects that are part of this program are provided in the bimonthly DOE newsletter, "Materials and Components in Fossil Energy Applications," published by Battelle-Columbus Laboratories.

Although not a participant on the AR&TD Fossil Energy Materials Program, Ceramtec, Inc. has been invited to contribute to this semiannual report in view of the relevance of the ceramic composite work being performed at that organization to similar work on the AR&TD Fossil Energy Materials Program. Their report, entitled "Design, Fabrication, and Interface Characterization of Ceramic Fiber-Ceramic Matrix Composites," is included on page 33. The Ceramtec project is sponsored by the Small Business Innovative Research (SBIR) Program.

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PART II - STRUCTURAL CERAMICS

ANL-1(A) - DEVELOPMENT OF NONDESTRUCTIVE EVALUATION
METHODS FOR STRUCTURAL CERAMICS

W. A. Ellingson, R. A. Roberts, N. Gopalsami, S. Dieckman
T. Hentea,* and J. J. Vaitekunas

Argonne National Laboratory
Materials and Components Technology Division
Argonne, Illinois 60439

INTRODUCTION

The purpose of this program is to (a) evaluate and develop acoustic, radiographic, and nuclear magnetic resonance (NMR) techniques for the nondestructive evaluation (NDE) of structural ceramics, with emphasis on characterization of formed (green-state) ceramic bodies to obtain information relevant to process control; (b) establish the types of characteristics (density gradients, organic binder/plasticizer distributions, inclusion distributions, etc.) that can be detected by NDE techniques; and (c) determine correlations between the presence of flaws, NDE results, and fracture behavior of densified ceramics. NDE techniques are being developed to detect porosity, cracking (surface and internal), inclusions, density variations, and binder/plasticizer distributions. The work encompasses monolithic ceramics and ceramic-ceramic composites. Parts of this task are correlated with Task ANL-1(B), which will be included in Task 1 reporting beginning with the next report.

DISCUSSION OF CURRENT ACTIVITIES

Work continued during this period on most aspects of the NDE development program, with emphasis on (a) development of the microfocus computed tomography (CT) scanner, (b) development of an NMR imaging accessory, and (c) correlation of acoustic microscopy data with fracture behavior. In addition, work continued on development of digital image processing.

*Purdue University-Calumet, Hammond, IN.

Microfocus Computerized Axial Tomography

Work to develop a high-resolution X-ray tomographic imaging station continued during this reporting period. The station, based on a micro-focus X-ray head, will serve as a tool for studying three different types of detectors: X-ray film, an image intensifier with digitizing video camera, and a solid state detector array. Each detector system will be used at different times to evaluate sensitivity.

During the current reporting period, we performed experimental work on the use of X-ray film, digitized by a scanning micro-densitometer, for acquiring and reconstructing CT images. We also performed initial hardware system development on the image intensifier with video camera. Steps were taken to obtain initial software for cone-beam reconstruction.

Our first CT experiments were conducted with a specially built test phantom (see Fig. 1). The test phantom consisted of a 50-mm-diam Lucite disk with a central 6-mm-diam shaft made of aluminum, two inserts of brass and stainless steel, and a thin lead outer covering. The experimental setup is shown in the photograph of Fig. 2. The X-ray film, Eastman Kodak Type M (a standard 8 x 10-in. film) in a vacuum pack, was placed on a flat surface at a distance chosen such that projections of the test phantom yielded a 2X magnification. Between the phantom and the film, a 2-mm collimator was built from heavy 100-mm-deep lead blocks. No collimation was done at the X-ray head. By allowing only a 2-mm strip of film to be exposed for each projection, we were able to record up to 36 projections on a single film pack.

The microfocus X-ray head was operated at 150-kVp accelerating voltage and 0.22 mA current. For each projection, the film was exposed for 18 seconds. Projections were taken at 10° intervals over 360°. For each projection, the test phantom was rotated by 10° and the film was translated by 4 mm.

INITIAL MICROFOCUS X-RAY COMPUTED
TOMOGRAPHY TEST PHANTOM
LUCITE DISC WITH INSERTS

Fig. 1

Drawing of Initial Test Phantom
Used for Microfocus CT Tests.

Fig. 2

Photograph of Microfocus X-Ray
CT System Showing Microfocus
X-Ray Head, Test Phantom, and
Detector.

The film was developed and dried, and then digitized with a light drum-scanner with a 200- μm fixed aperture. The digital projection data were transferred via Ethernet to our VAX 11/785 system. Two types of pre-reconstruction processing were performed: rotation and alignment. The projection data needed a rotation to ensure that each row of data corresponded to a slice through the phantom orthogonal to the central shaft. The alignment, both vertical and horizontal, was required to ensure that the projections corresponded to the same slice, and that the central ray of each projection back projected through the center of rotation.

The reconstruction of the cross section is based on the fan-beam space-convolution algorithm of Lakshminamayan and Naparstek. The geometry parameters of the reconstruction are defined in Fig. 3. The reconstruction process consists of the following three steps:

- (a) multiply the raw projection data by a weighting function, $d(K)$, where

$$d(K) = \frac{1}{\sqrt{1 + (K/\text{RFAN})^2}}$$

- (b) convolve the modified projection data with a particular convolution function, $c(K)$, where

$$c(K) = \begin{cases} \pi/4 & \text{if } K = 0, \\ -1/\pi K^2 & \text{if } K \text{ is odd,} \\ 0 & \text{if } K \text{ is even;} \end{cases}$$

and finally,

- (c) back project the modified and convolved data sets.

The process described above was carried out for the Lucite phantom. Thirty-six (36) views were used, with 10° rotation intervals. In order to initially compare image contrast, we set up the computer code so that any pixel value above 0 was set equal to 0 outside the boundaries of the test object. Figures 4 and 5 show the effects of setting zeros. Figure 4

shows the reconstructed object with zeros outside the boundaries and Fig. 5 shows the reconstructed object when no zeros are set outside the object. Clearly, suppressing noise outside the object adds to the clarity of the object boundary.

We also attempted to perform a CT reconstruction of the ceramic turbocharger rotor shown in Fig. 6, but were not successful because of poor density contrast near the blade tips. In relation to this experiment, two disadvantages of the film/scanner detector system are apparent. First, the nonlinear characteristic and the limited dynamic range of the film restricts its use to circularly symmetric quasihomogeneous objects. Second, the experimental setup required special care to ensure proper alignment of the projection data.

Fig. 3

Schematic Diagram Showing Details of Reconstruction Geometry Used in X-ray CT.

Fig. 4

Reconstructed Image of Test Phantom Shown in Fig. 1. 36 views over 360°; 200- μ m slice thickness.

Fig. 5. Same as Fig. 4, Except No Zeros Were Added to Suppress Noise Outside Object Boundaries.

Fig. 6. Photograph of Green-State Injection-molded Si_3N_4 Turbo-charger Rotor.

The future work on solid state detector arrays and on the image intensifier with video camera is expected to solve some of the problems encountered with the film/scanner system.

An X-Y- θ stage for the microfocus CT station was ordered during the current reporting period. This stage has stepping motors which will be controlled from the host computer for the station (an IBM-PC/AT). During the next reporting period, this stage will be installed and used to control the position of the test object during data acquisition (see Fig. 7).

Real-Time Radiography

As noted in our last semiannual report,¹ we have received and installed a Ridge HOMX-161 microfocus X-ray head. As a part of our radiographic imaging technology development effort, we will use the microfocus X-ray head for both X-ray computed tomographic imaging (with several different detectors) and real-time radiographic imaging (with an image intensifier system). During the current reporting period, we received (on loan) a 9-in. image intensifier from Precise Optics. We have chosen to use an available Sony CCD camera and monitor from the digital X-ray imaging facility for our initial work. As noted above, we will soon be installing an X-Y- θ stage which will be controlled from the IBM-PC/AT host control computer as shown in Fig. 7. In addition, the HOMX-161 microfocus X-ray head was interfaced to the host computer. Hard copies of initial real-time data were obtained via a Polaroid camera. We will soon be installing an Ethernet connection to allow the digitized data to be output to either a matrix camera (accessed via the Argonne computer network) or an available hard-copy output device which has a limited dynamic range (gray scale) of 64 (6 bits). The image intensifier screen (a 2-D detector) will also be explored for use as the detector system in a cone-beam (3-D) computed-tomographic imaging system.

Fig. 7. Schematic Diagram of Real-Time X-ray Imaging System.

Ultrasonic Methods

Work has continued on the application of ultrasonic backscatter microscopy for the detection of near-surface flaws in hot-pressed Si_3N_4 , and the correlation of NDE data with fractography results obtained under Task ANL-1(B). Since the last reporting period, four additional specimens of hot-pressed Si_3N_4 containing seeded Si inclusions have been prepared. Five modulus-of-rupture (MOR) bars were machined from each specimen. The tensile surfaces of the MOR bars were imaged with ultrasonic backscatter microscopy; the bars were then fractured in four-point bending, and the fracture surfaces examined under Task ANL-1(B). The NDE and fractography data were then correlated to determine whether the failure-initiating flaws had been detected by NDE.

In the first two specimen sets examined, fractography data revealed that approximately half of the failures were due to isolated silicon inclusions, whereas failure in the remaining specimens originated at machining-induced flaws or at failure sites that were not well defined.

As previously observed, the failure sites were successfully detected by NDE in those specimens for which an isolated near-surface flaw was clearly discernible by fractography, provided the local surface roughness was small enough to yield a sufficient signal-to-noise (S/N) ratio between signals scattered by the isolated flaw and the surface roughness.

In the examination of the third and fourth specimen sets, the spatial resolution of the ultrasonic scanning was increased to allow detailed imaging of the surface topography. With these higher-resolution images, it is easier to determine whether scattered signals originated at surface roughness or isolated inclusions. The higher resolution does not, however, improve the ability to identify isolated flaws that are positioned in locally rough areas. The detection of near-surface flaws in locally rough areas remains as a significant problem to be addressed.

The third specimen set studied had a relatively rough surface finish, hence few isolated near-surface flaws were identified by NDE. Later examination of the MOR bars prepared from this specimen set revealed that errors were apparently made in performing the surface finish, resulting in a greater-than-intended surface roughness. Even with the apparent error in surface finish, the surface roughness was less than what would be expected in routine ceramic processing. This underscores the difficulty encountered in detecting Si inclusions in Si_3N_4 because of the relatively weak ultrasonic scattering caused by this type of inclusion.

In the fourth specimen set examined, the desired surface finish was obtained, and as a result, the NDE results were quite good. The failure sites were unambiguously detected in 3 out of 5 MOR bars. An example of ultrasonic backscatter microscopy data obtained in the fourth specimen set is presented in Fig. 8. This image was obtained by using a 50-MHz, broadband transducer with a 0.5-in. focal length and 0.25-in.-diam lens in an -12° incident backscatter mode and 1.5 mm defocus. The image displays peak detected reflected amplitudes. The image covers 12.3 mm of the specimen with a $24\text{-}\mu\text{m}$ scanning resolution. Isolated near-surface flaws appear as crescent-shaped features, owing to the converging geometry of the surface wave field near the focal zone of the transducer.

Fig. 8. Ultrasonic Backscatter Microscopy Image of the Tensile Surface of a Si-seeded Si_3N_4 MOR Bar.

In an attempt to study specimens with isolated near-surface pores, work was performed on Si_3N_4 specimens machined from material (supplied by Norton/TRW) which was specified to be 95 to 97% dense. Two sets of specimens consisting of 5 MOR bars each have been examined with procedures identical to those applied to the Si-seeded specimens. Isolated near-surface flaws are clearly discernible in the NDE data. The fractography data indicated that 5 out of 10 specimens failed at near-surface pores. The fractography results in the remaining 5 specimens were ambiguous. Correlation of the NDE and fractography data indicated that NDE detected the failure-initiating near-surface pore in 3 out of these 5 specimens. It was noted, however, that the indications of the near-surface pores in the NDE data were not as pronounced as those obtained during the last reporting period in an examination of a specially prepared Si_3N_4 specimen seeded with nearly spherical 20-mm near-surface pores.¹ The failure-initiating flaws in these 5 bars were generally larger than 20 μm . This raises questions regarding (1) the structure, shape and composition of the near-surface pores observed in these 5 bars, such as whether each pore consists of a single void or a cluster of smaller voids, and (2) the sensitivity of ultrasonic microscopy to varying pore structures.

Obtaining Si_3N_4 specimens with isolated near-surface pores for fractography studies remains as a problem to be addressed.

Nuclear Magnetic Resonance Imaging

We are in the process of building necessary accessories to convert an existing 2.1-T NMR spectrometer into an imaging system. The facility, when built, can be used for both spectrometry and imaging experiments. Figure 9 shows a block diagram of the NMR imaging system under construction. The components that already exist are the Bruker CXP 100 pulsed NMR spectrometer, the Aspect 3000 computer that controls the spectrometer, and the 73-mm bore, 2.1-T superconducting magnet. The major components that are being built are (1) an imaging probe that excites the nuclear spins of a sample and detects their nuclear signal in a spatially encoded manner and (2) an IBM-PC-based pulse programmer that provides appropriate pulse sequences for driving the imaging coils. These pulses will be amplified by power amplifiers (RF and gradient amplifiers), the output of which drives the coils of the imaging probe. Three fast-switching power amplifiers, Techron Model 7570, have been procured for driving the x, y, and z gradient coils. The NMR data (in the form of detected RF signals) from the Aspect 3000 computer will be transported via the Ethernet local area network to a VAX 11/785 computer in another building where the image construction and processing will take place. Back-projection software has been obtained from Hare Associates and will be employed for reconstruction of NMR images.

Fig. 9. Block Diagram of the NMR Imaging System.

During the current reporting period, we concentrated on the design of the gradient coils, which constitute a major part of an imaging probe. The purpose of the gradient coils is to provide spatially varying magnetic fields $B_z(x)$, $B_z(y)$, and $B_z(z)$ with respect to the x , y , and z directions of the laboratory coordinates, where the main magnetic field B_0 is in the z direction. If the gradient fields are linear,

$$B_z(x) = \frac{\partial B_z(x)}{\partial x} x = G_x x \quad (1a)$$

$$B_z(y) = \frac{\partial B_z(y)}{\partial y} y = G_y y \quad (1b)$$

$$B_z(z) = \frac{\partial B_z(z)}{\partial z} z = G_z z \quad (1c)$$

Then the Larmor (resonance) frequency is spatially encoded as follows:

$$\omega(x) = \gamma(B_0 + G_x x) \quad (2a)$$

$$\omega(y) = \gamma(B_0 + G_y y) \quad (2b)$$

$$\omega(z) = \gamma(B_0 + G_z z) \quad (2c)$$

where γ is the gyromagnetic constant for the nuclei of interest. Thus, we need three gradient coils capable of producing linear gradient fields of magnitudes G_x , G_y , and G_z in the x , y , and z directions.

Coil Configuration and Spacing

The main issue in the design of linear gradient coils is to determine the coil geometry and the spatial distribution of the conductors that will produce the desired gradient fields in the imaging volume of interest. A common design procedure incorporates saddle-type coils for the x and y gradients and a pair of Maxwell coils for the z gradient, as shown in Fig. 10. Researchers have produced and tested optimal saddle coil designs, based on the theory of four infinite straight conductors situated on the circumference of a circular cylinder of radius a , and carrying currents in the same direction.^{2,3} We used the relationships given in

Ref. 1 to define the coil spacings in terms of the radius a , which we chose to be 3 cm; the results for the spatial dimensions of the saddle coil are shown in Fig. 10. For the spacing between the Maxwell coils of the z gradient, a value of $\sqrt{3}a$ yields the best gradient linearity.

Fig. 10. Gradient Coil Geometry. Dimensions in cm.

Calculation of the Gradient Fields

For the assumed coil geometry, we must calculate the field strength per ampere-turn as a function of spatial position in order to determine (1) the required ampere-turns for producing a desired gradient strength and (2) the imaging volume over which the fields are linear within a given tolerance. A 3-D computer code, OPEPA/TOSCA from Vector Fields Ltd., was used to calculate the field strengths. The magnitudes of the gradients in the y (or x) and z directions are plotted in Figs. 11 and 12, respectively, for a 10-A current in a three-turn winding of 0.39 x 0.039-cm cross section. The linear range of the fields for various tolerances is listed in Table 1.

Gradient Strength Requirements

The minimum required gradient strength, G_m , for a desired spatial resolution depends on (1) the inhomogeneity of the main magnetic field, and (2) the line width of the resonance (the latter may become an overriding factor in NMR imaging of solids). Assuming the first factor to be overriding,

$$G_m > \Delta B_i N / D = \Delta B_i / \text{pixel size} \quad (3)$$

where ΔB_i = maximum intrinsic magnetic field deviation from the central nominal value over the field of view, N = number of pixels across the image, and D = diameter of the field of view. Substituting $D = 2.5$ cm (1% linearity), $\Delta B_i = 5 \times 10^{-6} \times 2.1 \times 10^4$ G, and $N = 128$, G_m should be greater than 54 G/cm for a pixel size of 0.2 mm.

Fig. 11. Gradient Magnitude of x or y Field.

Fig. 12. Gradient Magnitude of z Field.

Table 1. Gradient Field Linearity

# Tolerance	Linear range of x or y field (cm)	Linear range of z field (cm)
1	± 1.2	± 1.0
2	± 1.4	± 1.3
3	± 1.5	± 1.5
4	± 1.6	± 1.6

Fig. 13. A Cross Section of the Winding. Dimensions in cm.

Determining the Number of Turns and the Wire Size

From the calculated value of 2.9 G/cm for 30 ampere-turns (see Fig. 11), a gradient strength of, say, 50 G/cm will require 514 ampere-turns. Since the gradient amplifier (Techron 7570) can only deliver 20 A maximum, the winding must have 26 turns. In the available spacing between the coil form and the probe housing, 24 turns of AWG 22 class H insulated copper wire can be accommodated as shown in Fig. 13. Epoxy glass, which has adequate strength and temperature resistivity, can be used for the coil form. The x (or y) and z coils cross at certain locations and the x and y coils overlap for certain lengths (see Fig. 10). In those cases, a

compromise on the width and thickness specifications of the winding is necessary and the wires will have to be distributed to fit in the limited spacing. In order to determine the effect of distributing the wires in the axial direction, the gradient fields resulting from 24 turns of 0.96×0.16 -cm cross section were simulated with a 20-A current. The field gradient at the center of the coils was 46.8 G/cm, and the linearity of the field nearly matched that of the 0.39×0.039 -cm winding (Fig. 11).

Cooling Considerations and the Duty Cycle

The dc resistance of the x (or y) coil for a 58.7-ft, 22 AWG copper wire equals 0.9Ω , and that of the z coil of length 29.9 ft is 0.5Ω . The total power loss in all the windings at a maximum continuous current of 20 A is 942.4 W. Assuming the power loss is distributed over a 10.5-cm length of the coil form, then the cooling area equals 198 cm^2 (30.7 in^2) and the power loss per unit area is 4.76 W/cm^2 (30.7 W/in^2). Forced-air cooling will be necessary to remove the resultant heat from the power losses in the winding. If we flow air at a velocity of 10 ft/s in the annular region between the coil former and the probe housing, the flow rate of air becomes 6.6 CFM. At a continuous rating (when the fields are on continuously at the maximum level), simple heat transfer calculations indicate a hot-spot temperature of 2074°C in the winding. But at a 5% duty cycle, we get an acceptable value of 132°C for the hot-spot temperature.

To test the switching speed of the gradient fields, we wound a 4-turn saddle coil set on a 6-cm-OD form and measured the inductance. The extrapolated inductance for a 24-turn coil conforming to our design will be 0.24 mH. The rise time for the current through the coil to reach its maximum of 20 A when driven by a 120-V power amplifier is calculated to be $32 \mu\text{s}$, which falls in the acceptable range.

Work is currently under way on the design of the RF coil and the associated matching and tuning circuits. Simultaneously, the fabrication of the coil formers and their supports inside the probe housing, as well as the actual winding of the coils, will be initiated. Work is also under way on the design and building of pulse programmer circuits and software.

Digital Image Processing

During the current reporting period, our efforts focused on networking the Central Image Processing Facility and on developing software. DECNET-DOS was installed on the imaging workstation and a 3COM hardware board was installed and connected to an Ethernet modem. This connection allows high-speed interactive communications and image transfer to the Argonne supercomputer/minicomputer network. X-ray images can be transferred back and forth between the supercomputer for numerical analysis and the imaging facility for viewing and filtering.

A software package was integrated to allow the imaging system to emulate a Tektronix graphics system, which enables us to run FTNMR (a VAX-based NMR reconstruction program). We also developed software to do a block-average data extraction (with a 2 x 2-mm block, in this case) from X-ray films. A significant feature of the software is that it allows us to place images at any angular orientation (in a horizontal plane) normal to the camera axis.

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ANL-1(B) - EFFECTS OF FLAWS ON THE FRACTURE BEHAVIOR
OF STRUCTURAL CERAMICS

J. P. Singh, A. L. Bosak, and C. Y. Chu

Argonne National Laboratory
Materials and Components Technology Division
Argonne, Illinois 60439

INTRODUCTION

The purpose of the work in this task is to characterize the fracture behavior of structural ceramics (Si_3N_4) with well-defined flaws. Specimens of Si_3N_4 with controlled flaws will be fabricated by introducing controlled amounts of pore formers and second-phase additions, such as Fe, Si, WC, and TiC. Nondestructive evaluation (NDE) methods will be used to locate the flaws, and fracture bars will be cut accordingly. The fracture stress, fracture toughness, and elastic modulus of these specimens will be evaluated to establish the effects of microstructural flaws on the fracture behavior of these structural ceramics. The findings will be correlated with the NDE data of ANL-1(A) to allow NDE inspection methods to be quantified.

DISCUSSION OF CURRENT ACTIVITIES

Effort during this period concentrated on fracture-NDE studies of hot-pressed specimens of Si_3N_4 -Si as well as sintered specimens of Si_3N_4 with and without controlled porosity. Specifically, work continued in three areas: (1) specimen preparation [hot-pressing, fabrication of modulus-of-rupture (MOR) bars, and grinding of the specimens to appropriate surface finish]; (2) mechanical properties measurement and fractographic evaluation of the fracture surface to locate critical flaws; and (3) establishment of correlations between critical flaws, mechanical properties, and NDE results.

Two disks of Si_3N_4 with 6% Y_2O_3 and 1% Si (with $\leq 149\text{-}\mu\text{m}$ particle sizes) have been hot-pressed in a boron-nitride-coated graphite die at 1725°C and $\sim 22\text{ MPa}$ for 2 h in a high-purity N_2 atmosphere. The disk

specimens were ~98% dense. Ten MOR bars were machined from these disks. These bars were surface ground to a 15-mm finish and were examined by NDE [backscatter ultrasound, Task ANL-1(A)] to determine the exact locations of possible critical flaws as discussed in Refs. 1 and 2. Subsequently, the bars were broken in a four-point bending mode, making sure that the critical flaws were located in regions of maximum tensile stress. The flexural strength was measured to be 625 ± 94 MPa. The fracture surfaces of the broken bars were evaluated by fractography to locate critical flaws and measure their sizes. The fractographic evaluations indicate that out of 45 specimens of Si_3N_4 -Si evaluated so far, the failures in 21 specimens initiated from Si-induced critical flaws. For these specimens, the critical-flaw locations predicted by NDE appear to correlate well with the locations determined by fractographic observations. In the other 24 specimens, the failure initiated primarily from the machining flaws.

Fracture mechanics calculations³ were performed to evaluate the critical flaw size for the 21 specimens in which failure appeared to have initiated from Si-induced flaws. A comparison of the calculated and fractographically measured flaw sizes indicated that the ratio of the calculated and measured flaw sizes generally varied between 1.17 and 4.5.

Fracture-NDE studies are also continuing on Si_3N_4 specimens with limited porosity. Four large specimens of Si_3N_4 with ~3-5% porosity (as indicated by the vendor) have been obtained from Norton/TRW, Northboro, MA. Several thin (~4 mm) disks were machined from one of the large specimens and 5 MOR bars were cut from each of two disks. These bars were given a 32- μm surface finish and were then examined by NDE to locate potential critical flaws and subsequently broken in a four-point bending mode. The average strength of the two sets of 5 bars was measured to be 405 ± 48 MPa and 311 ± 85 MPa, respectively. The corresponding values of the fracture toughness were measured to be 6.5 ± 0.3 and 6.33 ± 0.14 $\text{MPa}\sqrt{\text{m}}$, respectively. The difference in mechanical properties for the two sets of specimens is believed to be due to density differences. The fracture surfaces of the broken bars were examined by fractography. Critical flaws were unambiguously observed to be pore-like cracks in 5 of the 10 specimens examined. For 3 of these 5 specimens, the critical-flaw locations predicted by NDE showed good agreement with the locations determined by

fractographic observations. For the other two specimens, the correlation was ambiguous.

For the 5 specimens in which failure was observed to initiate from pore-like cracks, critical flaw sizes were also calculated by the fracture-mechanics approach. The ratio of the calculated and fractographically measured flaw (pore) sizes varied between 1.7 and 5.7 for the 17 specimens evaluated so far (including the results reported in Ref. 4).

Efforts are now under way to make green and dense composites of Si_3N_4 matrix with Si_3N_4 whisker reinforcement to initiate fracture-NDE studies on composites.

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DESIGN, FABRICATION, AND INTERFACE CHARACTERIZATION
OF CERAMIC FIBER-CERAMIC MATRIX COMPOSITES

C.W. Griffin, D.K. Shetty^a and D.W. Richerson

Ceramatec, Inc.
2455 South 900 West
Salt Lake City, Utah 84119

INTRODUCTION

This report describes the progress achieved on the second phase of a three-phase program to design and fabricate ceramic fiber/ceramic matrix composites that exhibit high strength and high fracture toughness at temperature up to 1200 °C in an oxidizing atmosphere. These composites will be designed by optimizing the fiber/matrix interface through characterization and control of the interfacial bond. The Phase I research established the experimental feasibility of a new modified pushout test and verified the supporting theoretical relations that permit determination of the interfacial properties these include the shear debond strength, the sliding friction shear stress, the residual compressive stress, and the coefficient of sliding friction. The Phase II objectives are directed towards use of the Phase I test and analysis methods to effectively develop improved composites and to better understand the role of the fiber-matrix interface in composite properties. The following specific objectives will be achieved in Phase II.

1. Achieve increased understanding of interface characteristics versus chemistry, strength, fracture toughness, matrix cracking limit and temperature stability in an oxidizing atmosphere.

^aA consultant associated with the Materials Science Department at the University of Utah, Salt Lake City, Utah.

2. Demonstrate a fiber-reinforced ceramic which fractures in a composite mode and retains its composite behavior to at least 1200 °C in an oxidizing environment.
3. Achieve a high toughness fiber-reinforced ceramic composite with no matrix cracking below a stress of 400 MPa.
4. Demonstrate 500 hours stress rupture life at a stress of 200 MPa at 1000 °C and demonstrate by post-exposure fracture that composite fracture behavior has been retained.

Phase II of this project is supported by the Department of Energy's Small Business Innovation Research Program Office.

DISCUSSION OF CURRENT ACTIVITIES

Work during this period centered on modifying equipment initially developed in Phase I, developing pushout specimen fabrication procedures, fabricating pushout specimens, performing pushout tests and subsequent data analysis, and fabricating and evaluating the bulk properties of a composite consisting of a low expansion ceramic matrix reinforced with a large volume fraction of SiC fibers. The results of these activities are described in Tasks 1.0 and 2.0 below.

Task 1.0 Baseline Technology Development

The objectives of this task are to modify the equipment developed during the Phase I project, to develop procedures to fabricate the pushout test specimens and bulk composites, and to review the composite literature.

The fiber winding device has undergone several modifications since it was initially constructed in Phase I. The device has been modified to include a separate apparatus to guide the fiber onto the mandrel and to control the spacing between the fibers. In addition, a bracket was added to hold the fiber supply spool. Two further modifications are

planned. The first will allow the fiber to be wound onto the mandrel under a constant and controlled tension. Currently, the tension is applied by the operator. The second modification will add the capability of coating the fiber with a matrix slurry prior to winding the fiber onto the mandrel.

The micropositioner, used to position the specimen during the pushout tests, was modified to include a sliding stage and microscope mounted on an x-y stage to more easily align the fibers under the indenter and to view the pushed out fibers at the testing machine^a without removing the specimen. Previously, the fibers were aligned with the indenter at a separate location away from where the fibers were actually pushed out, which made the alignment procedure tedious and time-consuming. The present setup also allows the selected fiber to be viewed immediately so that minor position adjustments can be made during the test to keep the indenter centered on the fiber. The modified apparatus also reduces the operator strain.

The matrices selected for study in this project were Si_3N_4 , mullite, and a low expansion ceramic being developed at Ceramtec. An existing procedure was used to hot press Si_3N_4 . However, the hot pressing procedures to produce dense mullite and Ceramtec's low expansion ceramics had to be developed.

A procedure was developed to fabricate dense single-phase mullite. Two sources of mullite powder were examined: a powder available from a commercial vendor^b and a mullite powder produced through a sol-gel process at Ceramtec. The potential advantage of the sol-gel mullite was that it offered lower hot pressing temperatures, which would minimize fiber degradation and fiber-matrix interaction.

^aInstron model 1123, Instron Corp., Canton Ma.

^bHigh purity mullite grade 193 CR, Baikowski International Corp., Charlotte, NC.

Initially, the commercial mullite powder was hot pressed into a monolith with 88 % of theoretical density (TD) at 1350 °C, but higher densities are required for composite applications. By increasing the hot pressing temperature to 1450 °C, this powder densified to 98 %TD. X-ray diffraction (XRD) analysis indicated that the hot pressed sample was a single mullite phase. These results were used in Task 2.0 to prepare mullite specimens for pushout tests.

The sol-gel mullite powder could be hot pressed to 92 %TD at 1250 °C; however, X-ray diffraction (XRD) analysis of the hot pressed sample revealed the presence of an unidentified second phase. The intensity of the unidentified XRD peaks increased when the sample was heat treated at 1250 °C for 12 h and 1275 °C for 24 h. Additional work could not eliminate the second phase. While degradation of the fibers at temperatures in excess of 1400 °C is a concern, we feel it is more important to work with a matrix material of known composition and crystal structure. Therefore, we will restrict our work to the commercially available mullite powder.

Task 2.0 Interface Screening Studies Using Avco SiC Fibers.

The objective of this task is to screen potential matrix materials by measuring the properties at the fiber/matrix interface through the pushout tests and by preliminary evaluation of the bulk properties of composites with high fiber loading. Pushout tests were conducted on Si_3N_4 composites and a composite containing the low expansion ceramic. Composites containing the low expansion ceramic matrix were also evaluated for their bulk properties. In addition, pushout specimens were prepared with a mullite matrix.

Pushout Specimen Fabrication

All of the pushout specimens to be examined in this program will be made by hot pressing flexible fiber tapes between layers of the matrix powder. The tape will keep the fibers aligned during fabrication of the pushout specimens. This flexible fiber tape is produced by winding the SiC fiber^a around the mandrel of the fiber winding device at a spacing of about one-fiber diameter between fibers. The wound fibers are coated with an organic binder. After drying, the fiber/binder sheet is peeled from the mandrel and cut into individual tapes that fit into the hot press die.

Pushout Test Procedure

The procedure used to obtain the pushout data and to analyzed the data via the shear lag and linear models are described fully in the final report of the Phase I project¹. A short description of the experimental procedure is given here.

The pushout tests were carried out on a universal testing machine using the micropositioner to support and position the specimen under a specially-fabricated carbide tool for pushing the fibers out of the matrix. The carbide tool or indenter was fabricated from a WC-Co drill blank by grinding a conical tip with an included angle of 30° and a flat circular end approximately 50 μm in diameter.

A typical experiment consisted of making a light indent at some arbitrary location on the pushout specimen. The micropositioner and specimen were then slid under a stereo microscope and the initial indent was centered under the cross hairs of the eyepiece by adjusting the x-y stage of the microscope. After locking the microscope in position, the x-y stage containing the specimen was adjusted to locate a fiber

^aAll of the fibers discussed in this report are SCS-6 SiC fibers from Avco Inc., Lowell, MA. This fiber is coated with a double layer of carbon.

under the microscope crosshairs. The micropositioner and specimen were slid back under the carbide tool. The carbide tool in the crosshead was lowered at a constant rate of 5 $\mu\text{m/s}$ while the loads during debonding and pushout were continuously recorded. The debonding (P_d) and maximum pushout ($P_{\max}$) loads were determined from at least five measurements at each specimen thickness.

The interfacial properties:

T_d = Debonding shear stress, MPa

μ = Interfacial sliding coefficient of friction

σ_o = Residual compressive stress, MPa

T_f = Interfacial shear stress ($\mu\sigma_o$), MPa

where determined from a shear-lag analysis of the debonding and pushout loads measured during the pushout test for different embedded fiber lengths (L). A nonlinear regression analysis was used to determine the coefficients that describe the debonding and pushout loads as a function of fiber length by:

$$P_d = A \tanh(BL) \quad (1)$$

$$P_{\max} = C[\exp(DL) - 1] \quad (2)$$

where

$$A = (\pi d_f T_d) / \alpha \quad (3)$$

$$B = \alpha \quad (4)$$

$$C = (\pi d_f^2 \sigma_o) / 4k \quad (5)$$

$$D = (4\mu k) / d_f$$

and

$$k = (E_m v_f) / E_f (1 - v_m) \quad (6)$$

where d_f is the fiber diameter, E and v are, respectively, the elastic modulus and Poisson's ratio of the fiber (f) and matrix (m). Linear models for debonding and pushout were also used to determine T_d and T_f from the pushout data.

Interfacial Properties of Si_3N_4 Composites

Silicon nitride billets were hot pressed at 1750 °C for 1 h with either 5 wt% MgO or 6 wt% Y_2O_3 -2 wt% Al_2O_3 densification aids. These billets contained the SiC fiber tapes that were described in a preceding paragraph. The powder preparation and hot press conditions used were existing procedures developed at Ceramtec on previous programs. Pushout specimens were cut to various lengths from the hot pressed billets.

Typical loads for debonding (P_d) and fiber pushout ($P_{\max}$) as a function of embedded fiber length for Si_3N_4 -6 wt% Y_2O_3 -2 wt% Al_2O_3 specimens are shown in Figures 1 and 2, respectively. Data for Si_3N_4 -5 wt% MgO specimens were similar. The results of the shear lag and linear analysis are given in Table 1. The interfacial properties of a composite of Si_3N_4 -8 wt% Y_2O_3 -4 wt% Al_2O_3 containing SiC fibers^a determined during the Phase I program¹ are shown in Table 1 for comparison. Note that the fiber in this composite was not SCS-6 SiC fiber but rather the SCS-2 fiber.

The shear lag analysis of the pushout results for the Si_3N_4 -6 wt% Y_2O_3 -2 wt% Al_2O_3 and Si_3N_4 -5 wt% MgO matrices indicates that the debonding and frictional shear stresses are slightly higher for the Si_3N_4 /MgO matrix. The residual compressive stress in the Si_3N_4 -6 wt% Y_2O_3 -2 wt% Al_2O_3 system was three times higher than in the Si_3N_4 -5 wt% MgO system, although the coefficient of sliding friction was lower for the Si_3N_4 / Y_2O_3 / Al_2O_3 system. The cause of the higher residual compressive stress in the MgO system is not clear at this time, assuming that the different hot pressing aids do not greatly affect the thermal expansion of Si_3N_4 .

^aProvided by Battelle Columbus Laboratories, Columbus Ohio. The fiber used in this composite was Avco grade SCS-2.

Figure 1. Debonding load as a function of embedded fiber length (mm) for Si_3N_4 -6 wt% Y_2O_3 -2 wt% Al_2O_3 matrix reinforced with SiC fibers.

Figure 2. Maximum fiber pushout load as a function of embedded fiber length for Si_3N_4 -6 wt% Y_2O_3 -2 wt% Al_2O_3 matrix reinforced with SiC fibers.

Table 1. INTERFACIAL PROPERTIES OF Si_3N_4 MATRIX-SiC FIBER COMPOSITES

Composition, wt%				Hot Press Temp. °C	Debonding Shear Stress, MPa	Residual Compressive Stress, MPa	Coefficient of Sliding Friction	Frictional Shear Stress, MPa
Si_3N_4	Y_2O_3	Al_2O_3	MgO					
88 ^a	8	4	-	1700	12.9 (7.7) ^b	178	0.06	10.7 (11.8)
92 ^c	6	2	-	1750	2.6 (2.6)	158	0.01	1.6 (2.5)
95 ^c	-	-	5	1750	5.7 (5.7)	49	0.07	3.4 (6.3)

^aObtained from Battelle Columbus Laboratories, contained Avco SiC fiber Grade SCS-6.

^bLinear analysis in parens.

^cReinforced with SCS-6 Avco fibers.

The linear model predicts similar debonding and frictional shear stresses for Si_3N_4 -6 wt% Y_2O_3 -2 wt% Al_2O_3 composite and similar debonding shear stresses for the Si_3N_4 -5 wt% MgO specimens. However, the frictional shear stress obtained via the linear model is higher for the Si_3N_4 -5 wt% MgO composite than determined by the shear lag analysis. The frictional shear stress is even higher than the debonding shear stress, which makes the linear analysis of this data suspect.

The difference in the interfacial properties between the Si_3N_4 matrix containing 8 wt% Y_2O_3 and 4 wt% Al_2O_3 (from Battelle) and the Si_3N_4 -6 wt% Y_2O_3 -2 wt% Al_2O_3 matrix is probably due to the different fibers used. For the Battelle samples, the debonding shear stress, the frictional shear stress, and the coefficient of friction were all higher than the measured corresponding values in the Si_3N_4 -6 wt% Y_2O_3 -2 wt% Al_2O_3 system. The residual compressive stress was slightly higher for the Si_3N_4 -8 wt% Y_2O_3 -4 wt% Al_2O_3 system. There are three possible causes for the differences observed between these two systems: 1) different hot pressing aids, 2) different hot pressing temperatures, and 3) different fibers. A small change in the hot pressing aids would not be expected to result in such large changes in the interfacial properties especially in light of the fact that a completely different hot pressing aid (MgO) did not effect as large a change. The lower hot pressing temperature would be expected to decrease the fiber-matrix bond of the Battelle specimens rather than increase it.

The type of coating applied to the fibers can have a significant effect on composite properties^{2,3}, and recently it has been shown that the coating thickness can also affect composite properties^{4,5}. While both types of fibers have carbon-rich coatings on their surfaces the coating on the SCS-6 fiber is a double carbon layer 3 μm thick compared to single 1 μm coating on the SCS-2 fiber⁶. These coating thicknesses appear to be affecting the interfacial properties of these

Si_3N_4 composites. The thinner carbon coating on the SCS-2 fiber allows the fiber and matrix to become more strongly bonded resulting in a high debonding shear stress as shown in Table 1 for the composite containing the SCS-2 fiber. As the fiber is pushed out of the matrix, the SCS-2 fiber requires a higher frictional shear stress mainly due to the higher coefficient of friction, which may be influenced by the fiber/matrix bond.

In the future, higher volume fraction composites will be prepared under the same conditions as the pushout specimens and evaluated to correlate the interfacial properties with the bulk composite properties such as strength and fracture toughness. In addition, SCS-2 and SCS-8 fibers have been ordered and will be examined. The SCS-8 fiber has a silicon rich coating on the surface. Alternate coatings as well as changes to the matrix composition will be examined to determine their effect on interfacial and bulk composite properties.

Interfacial Properties of SS50 Composite

One matrix material being examined in this program is based on compositions from the $\text{NaZr}_2\text{P}_3\text{O}_{12}$ (NZP) system. These materials offer near-zero thermal expansion, potentially higher temperature capability, and lower elastic modulus than lithium aluminum silicate (another material used for low thermal expansion applications). One composition from the NZP family was selected for the initial work in this program. The exact composition of this material, designated SS50, can not be reported until patent applications are filed.

A billet containing the unidirectionally aligned SiC fibers in an SS50 matrix was hot pressed at 1300 °C for 0.3 h. The density of the hot pressed billet was above 95 %TD. This billet was cut into smaller samples for pushout tests. The fibers contained in the SS50 matrix could be easily pushed out of the matrix during sample preparation and special care

had to be taken to avoid debonding the fibers and pushing them out. Debonding and pushout data were obtained from specimens containing embedded fiber lengths between 1 and 8 mm. There was a large amount of scatter in the data up to 4-mm embedded fiber length; the standard deviation was nearly as large as the average measured load. The loads to debond and pushout the fibers were very small, e.g., around 1 N or less. In comparison, the loads required to debond and pushout fibers in a Si_3N_4 matrix would be greater than 10 N for an embedded fiber length of 8 mm. At this time, additional data are needed to determine the interfacial properties via pushout tests of this composite system. However, a preliminary analysis of the data on hand indicates the debonding shear stress and frictional shear stress are less than 1 MPa, which is very low compared to the data in Table 1. Additional samples are being prepared at lengths greater than 8 mm for pushout tests during the next reporting period.

The limited interface bond is attributed to a synergistic effect between the fiber/matrix bond strength and thermal expansion mismatch. The moderate hot pressing temperature (1300 °C), the short time at temperature, and possibly the composition of SS50 minimizes the bond between the fiber and matrix. The thermal expansion mismatch between the fiber ($4.5 \times 10^{-6}/\text{C}$) and matrix ($1.6 \times 10^{-6}/\text{C}$) results in tensile stresses at the interface as the composite is cooled from the fabrication temperature. The minimal fiber/matrix bond combined with the stresses due to fiber/matrix expansion mismatch could lead to partial or complete debonding resulting in the weak fiber/matrix interface as indicated by the low shear stresses required to debond and pushout fibers in this system.

Bulk Properties of SS50 Composite

Based on the results discussed in the previous paragraph, an SS50 composite with higher volume fraction of SCS-6 fibers

was prepared and evaluated with regard to flexure strength. This composite was prepared by winding the SCS-6 SiC fibers around a hexagonal mandrel. A slurry, consisting of SS50 powder in an organic binder system was painted onto the fibers while they were still wrapped around the mandrel. After drying, the coated fibers were removed from the mandrel as a single sheet, cut into squares, and ten squares were stacked onto a 10-g bed of SS50 powder in a graphite hot press die. Another additional 10 g of SS50 powder was placed on top of the coated fibers to provide a matrix overburden during hot pressing. The composite was hot pressed at 1300 °C for 0.3 h in an argon atmosphere. The hot pressed billet was cut into six bars each approximately 4.5 x 5.5 x 44 mm. These bars were ground and five of the six bars were initially tested in 3-point bending. The cross-section of one bar indicated that the fiber loading was between 9-11 vol%.

The stress-crosshead displacement curve for a typical test is shown in Figure 3. The average first matrix cracking stress was 245 MPa. As shown in Figure 3, there was a large drop in stress when the matrix first cracked. This was followed by an increase in stress with further crosshead displacement, which indicates that the fibers were bearing the load as the composite strain increased. Ideally, the drop in stress following the first matrix crack should be a minimum.

Further tests described in this paragraph indicate that the magnitude of the stress drop after matrix cracking is dependent on the thickness of the matrix overburden. Examination of the five test bars indicated that more than 1 mm of the matrix overburden remained after grinding. The sixth bar was re-ground to remove more of the matrix overburden and then tested in 3-point bending. The matrix overburden was well less than 1 mm in the sixth bar tested.

This bar contained 9 vol% SiC fibers^a. The first matrix cracking stress for this specimen was 270 MPa and there was only a small drop in stress following the first matrix crack as shown in Figure 4. At this point in the test, the specimen was unloaded and visually examined. Two faint cracks were observed in the tensile surface. Both cracks had propagated through the matrix overburden (some remained even after additional grinding) towards the fibers following a path perpendicular to the longitudinal-fiber direction. As the cracks encountered the fiber reinforced matrix, they were deflected such that they followed a path parallel to the longitudinal-fiber direction. The crack path was only visible for a few millimeters after being deflected, which indicated crack propagation was arrested by the fiber reinforcement. The cracked composite was returned to the bend fixture and the load reapplied as shown in Figure 4. The stress supported by the cracked composite continued to increase with crosshead displacement reaching a maximum flexure stress of 344 MPa, which exceeded the matrix cracking stress (270 MPa). During the testing that followed the first matrix crack, sharp drops in stress were observed as shown in Figure 4. These drops are attributed to additional cracks developing in the matrix. No evidence of the fiber fracture was observed under visual examination. Eventhough all six composites tested were badly cracked after the 3-point bend test, none failed completely. The stress-displacement behavior shown in Figure 4 is the type sought after in fiber reinforced ceramic matrix composites.

A single bar was cut from the hot pressed billet used to prepare the pushout specimens, polished, and tested in 3-point bending to determine the strength of the matrix and to get an

^aWhile the volume fraction would be expected to increase as the matrix overburden was removed, this particular bar was cut from one side of the billet and as such did not have fibers through the width of the bar, which resulted in low fiber volume fraction.

Figure 3. Stress versus crosshead displacement for an SS50 composite with a large amount of matrix overburden. (a) matrix cracking stress.

Figure 4. Stress versus crosshead displacement for an SS50 composite with most of the matrix overburden removed. (a) first matrix cracking stress, (b) sample unloaded for visual examination, and (c) maximum flexure stress.

indication of fiber pullout during bending. The flexure strength of this bar was 97 MPa. While the bar only contained seven fibers, it was still able to support a stress of 20 MPa after the matrix had cracked. The fracture surface contained some fiber pullout, which will be examine in the scanning electron microscope (SEM) during the next reporting period.

A significant amount of strengthening occurs when the SS50 matrix is reinforced with SiC fibers. The monolithic strength (97 MPa) was increased to 278 MPa for a composite with about 10 vol% SiC fibers.

During the next reporting period, the microstructure of the SS50 composites will be examined. Additional SS50 composites containing much higher volume fraction of fibers (approaching 50 vol%) will be fabricated and evaluated. In addition, two other N2I compositions will be examined to better determine the effect of thermal expansion. One composition will have coefficient of thermal expansion greater than the SiC fiber, while the other will be less than the SiC fibers.

Mullite Composite Fabrication

A mullite billet was hot pressed at 1450 °C for 0.3 h to a density of 98 %TD. This billet contained unidirectional SiC fibers between layers of mullite powder. This billet was cut into smaller specimens for pushout tests. These tests will be conducted during the next reporting period.

Plans for Next Reporting Period

Due to the promising results obtained this quarter, work on the SS50 composite system will be emphasized. The second priority will be to fabricate and examine Si_3N_4 -based composites that contain a high volume fraction of fibers. The third priority will be given to determining the interfacial properties of mullite matrix composites. The

following work elements, in order of their priority, are planned during the next quarter:

1. Fabricate and evaluate SS50 composites that contain a high volume fraction of SiC fibers.
2. Examine the microstructure and fracture surfaces of SS50 composites.
3. Determine the elastic modulus, flexure strength, and coefficient of thermal expansion for hot pressed SS50 matrix only.
4. Complete fabrication trials of SS50 composite containing Nicalon fibers.
5. Complete additional pushout tests on SS50 composite system.
6. Prepare other NZP-based composites to examine the effect of matrix thermal expansion on interfacial and bulk composite properties.
7. Prepare Si_3N_4 composites with high volume fraction of SiC fibers for evaluation in the fourth quarter.
8. Complete pushout tests on mullite composites.

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GT-1 - DEVELOPMENT OF ADVANCED FIBER-REINFORCED CERAMICS

T. L. Starr, J. N. Harris, G. B. Freeman,
D. L. Mohr and J. S. Lyons

Energy and Materials Sciences Laboratory
Georgia Tech Research Institute
Atlanta, Georgia 30332

INTRODUCTION

The objective of the program is to develop an understanding of the critical factors in composite processing and to use this improved understanding to develop a silicon nitride composite microstructure for increased fracture toughness. The critical factors to be addressed are the nitriding process, the fiber-matrix interface, and processing-induced fiber orientation and residual porosity.

DISCUSSION OF CURRENT ACTIVITIES

Efforts this period have focused on review of methods for characterizing the fiber-matrix interface and development of a computer controlled furnace system for optimizing the reaction sintering process.

Characterization of Ceramic Composite Interfaces

A number of different technologies exist which utilize composite materials where the chemistry, morphology and crystallography of the interfacial phase(s) is of critical importance. The performance of heterogeneous catalysts, microelectronic devices, polymeric composites, metal matrix composites and ceramic composites all depend critically on the properties of a region which might be only a few nanometers or even angstroms in width. Both polymeric and metal matrix composites utilize reinforcing fibers which are expected to add strength and therefore need a strong bond between the reinforcing phase and the matrix materials. Ceramic materials are already strong and so, in this case, the reinforce-

ment phase is intended to provide increased toughness rather than additional strength. Therein lies the reason for quite different expectations of the matrix/second phase interfacial region for ceramic composites.

It is well known that ceramics exhibit brittle behavior and are subject to catastrophic failure. The establishment of a weakly bound second phase fiber or whisker is expected to provide significant increases in toughness via the mechanisms of crack branching, deflection and bridging. In order to tailor the interfacial region, numerous studies have commenced and are underway to explore the effects of different thin fiber coatings on bonding properties and subsequent macro-mechanical properties.

The ideal coating system will certainly differ for specific composite systems and may well necessitate multiple coatings. Lewis and Rice¹ suggest that a plausible coating system for a ceramic fiber/ceramic matrix composite would incorporate: 1) a diffusion barrier on the fiber; 2) a controlled strength layer, e.g., platinum; 3) a second diffusion barrier, and 4) a bond layer to provide adherence to the matrix. With one or more coatings, it is imperative that the coatings do not degrade the fiber mechanical properties nor that the coatings themselves degrade under processing or usage conditions.

Characterization Techniques

The characterization of interfaces takes place at a number of levels; the first of which encompasses the measurement of bulk properties and using those results to indirectly extract information about the interfacial region. Examples of this include traditional mechanical tests (e.g. three and four point bending tests) wherein the composites are processed in such a way that the only difference between samples is intended to be due to different fiber coatings which are deposited typically via chemical vapor deposition. Differences in the bulk properties are then interpolated back to what is known about the fiber surface treatment and conclusions drawn.

The difficulty with this process is the large number of unknowns and assumptions which must be made. When dealing with ultra-thin coatings down to a few nanometers in thickness, direct characterization of the coatings is the only way to determine, with maximum confidence, the structure and

chemistry of the interphase(s) present. The presence of impurities and minor elements (such as sintering aids like yttrium, calcium and iron oxides) along with sample density and processing environment can play major roles which transcend the behavior of the initial fiber coating. Lowden et al.² point out that the correlation of mechanical properties to interfacial phenomena is a complicated task. Nonetheless, if optimum tailoring of interfaces in ceramic composites is to be realized, it is imperative that the influence of different parameters is understood.

In order to examine directly the mechanical properties of the two phase composite, macroscopic model systems have been employed using a sandwich of planar materials. Oh et al.,³ for example, fashioned a double-cantilever-beam system comprised of a thin copper film bonded between silicate glass substrates with loading grips attached by epoxy. Using the grips, shear forces could be applied and crack growth studied. Morozumi et al.⁴ fashion Nb-Al₂O₃-Nb rods for tensile testing and for sectioning. Subsequent characterization of the fracture surfaces yields direct, readily available information about relative bending strengths and failure modes. This type of testing is, of course, a radical change in geometry from the curved surfaces of fibers and whiskers and may not model actual interfacial stresses very well.

Coyle et al.⁵ used a straightforward rule of mixtures approach to give the relationship between the bulk shear strength, the matrix shear strength and the shear strength of the interface as:

$$\sigma_{\text{bulk}} = X\sigma_{\text{interface}} + (1-X)\sigma_{\text{matrix}}$$

where X is the fraction of the shear crack surface area which is fiber/matrix interface.

In order to measure the toughening effects of a limited number of fibers, Fuller et al.⁶ loaded one, two and three fibers in a planar array along the crack front. Using a double cleavage drilled compression configuration, toughening increments have been measured as a function of fiber number and fiber coating.

Micromechanical tests can be extremely useful and are often quite clever in their conception. In practice, however, they are limited by

burdensome assumptions and tricky experimental technique. Marshall⁷ introduced an indentation method for measuring matrix-fiber frictional stresses in ceramic composites. This test uses a Vickers pyramid micro-indenter to push a fiber into the matrix and thereby measure both bond fracture strength and sliding friction. In this process, a polished cross section is prepared to yield a surface exposing fiber cross sections normal to the fiber axis. If the sample thickness (t) is less than the slipping distance of the fiber (l , which is essentially the length of the fiber) then the force balance can be explained by $F=2\pi Rt\tau$ where F is the applied force, τ is the frictional stress, and R the fiber radius. In practical samples, the sample thickness will be much greater than the slipping distance in which case part of the applied load is supported by the matrix. Neglecting fiber expansion, etc. it can be shown that

$$\tau = (2a^2H)^2 / (4\pi^2 u R^3 E_f)$$

where H is the fiber hardness, $2a$ is the length of the diagonal of the indentation on the fiber end, u is the displacement of the fiber and E_f is the Young's modulus of the fiber. The fiber hardness is typically measured on longitudinally exposed fiber cross sections in the same polished specimens.

It is, perhaps, more realistic to examine the fiber/matrix interface failure under conditions of strain rather than compression and the theory of this experiment has been discussed in several papers^{8,9,10,11}. In this configuration, a single long fiber is partially enclosed in matrix material and the uncoated end of the fiber is clasped. Stresses and strains monitored as the fiber is pulled from the matrix. Statistical deviations in the strength of individual fibers and the difficulty of working with such small specimens make this experiment fairly difficult. The micro-mechanical facilities at Georgia Tech are unique and would be useful in this particular analysis.

Lowden and Stinton¹² used multiple matrix cracking concepts to measure interfacial frictional stress. Since fibers in ceramic composite systems generally have a higher strain to failure ratio than that of the matrix, stressing coated fibers will cause the brittle matrix to fail before the

fiber. After a coating is applied to the fiber, the fiber is gripped on two uncoated ends and stressed resulting in repeated fractures of the ceramic coating until uniform lengths of unfractured coating are left on the fiber. Starting with the relationship

$$\sigma_{cg} = F/A_{cg}$$

where σ is the axial stress in the coating, F is the applied force and A is the area of the coating, the shear τ_i may be expressed as

$$\tau = \sigma_{cg}(d_c^2 - d_f^2)/2d_f l_c$$

where d_c is the diameter of the coating, d_f is the coating of the fiber and l_c is the critical length of fracture segment. In this experiment, it is essential that the fiber segments be examined while the fiber(s) are under tension so that the segments will not close and/or spall.

Traditional analytical examination of ceramics and composites often turns, sooner or later, to x-ray diffraction (XRD) which is used to produce qualitative and quantitative information about the crystalline phases found in a material. Depending on the mode of sample preparation (for analysis), information may also be available on preferred crystalline orientation within a sample. In the case where enough coating or interfacial material is present (ca. 1%) and that phase(s) is crystalline, XRD may be used to identify the phase(s) present. However, no information is available from XRD in this application on relative position of phases within the given composite system.

Probably the most common form of direct observation of fiber/matrix interfaces is with a scanning electron microscope. In this case, sample cross sections are examined either after fracture or in polished form. Fracture surfaces provide an immediate qualitative measure of toughness in that the fracture surface morphology is indicative of the mode of fracture. That is, the smoother the fracture surface the more likely that the failure was a brittle transgranular fracture while a roughened fracture surface with significant amounts of fiber pull out implies a toughened structure.

Direct observation of the fibers which have pulled out yields information about fiber degradation and, if the coating is thick enough, the integrity of the coating. Likewise, examination of the trenches from whence fibers have been pulled produces similar qualitative information. It is also possible, in many cases, to "see" the extent of fiber/matrix bonding by observing the boundaries at which the fibers and matrix meet. Polished cross sections are more amenable to quantitative examination where coatings may be analyzed (assuming they are thick enough) by energy dispersive x-ray spectroscopy and image analysis (for fiber deformation, bonding extent, etc.). An electron microprobe enjoys greater energy resolution and sensitivity x-ray analysis and, as such, offers "better" information than energy dispersive x-ray spectroscopy, but fundamentally the same type of information.

X-ray microanalysis of bulk samples is limited to a spacial resolution of about one cubic micrometer due to the physics of the scatter and mean free paths of x-rays. In order to garner data with better spacial resolution it is necessary to turn to other techniques. In the last two decades, surface analytical techniques have been brought to bear on this and other problems despite the significant inherent problems with these techniques.

Auger electron spectroscopy (AES) is an attractive technique which is, in many respects, very similar to x-ray energy dispersive spectroscopy coupled with an SEM. Both are electron beam techniques which can be focussed to fairly small spots and which can produce analytical maps. In addition Auger, in conjunction with an ion beam sputterer, can produce depth profiles wherein the composition of a sample is sequentially monitored as a function of depth (material removed by ion beam sputtering). Depth profiling is possible because the depth of analytical penetration of the AES technique is only a few nanometers. Unfortunately, AES resolution is limited to about 300 Å by the generation of enough electrons to get reasonable signal to noise. However, the major limitation with AES is the inability of the technique to handle nonconducting specimens.

Silicon carbide is a conductor and, as such, silicon carbide fiber reinforced materials are often conducting enough to allow AES analysis of the fibers and fiber trenches in situ. In this case, AES can be a powerful

tool to search for remnants of matrix on fiber or vice versa or to compare the elemental composition and structure of the fiber after processing to that as-coated.

X-ray photoelectron spectroscopy (XPS), a.k.a. electron spectroscopy for chemical analysis (ESCA), is a second surface analytical technique which is able to work with many non-conductors and which can often give information about the chemical state of a surface in addition to offering the capability to depth profile thin films. XPS's greatest limitation lies in its poor lateral resolution limited to tens of micrometers at best. XPS has been used productively to analyze the surfaces of fibers prior to coating and after coating but is of little use after the fibers have been incorporated into a composite. Imamura et al.¹³, for example, used XPS to examine differences in the oxygen content on Si_3N_4 powder surfaces as a function of powder preparation (i.e. wet or dry ground). In the case where the matrix could be dissolved preferentially, leaving the fibers, it might be possible to get useful information about the changes in the fiber/coating exterior chemistry, but the interpretation of the data would have to be done very carefully in order to avoid effects of the dissolvent.

In some respects, secondary ion mass spectrometry (SIMS) is the most attractive of the three techniques incorporating a scanning capability, a chemical differentiation capability and excellent elemental sensitivity. XPS and AES are limited to the detection of elements present to about 0.1% while SIMS is capable, in some cases, of detection limits down to parts per billion. The technique, which uses an ion beam to sputter off surface material into a mass spectrometer, is amenable to insulators as well as conductors and lends itself to both depth profiling as well as mapping. Unfortunately, the lateral resolution of the technique has not approached that of AES limiting the application of the technique with respect to systems with micro-domains. However, a new ion processing technique has been applied which has produced manufacturer's claims of a new generation SIMS with resolution comparable to that of AES with much greater sensitivity and information potential. If these claims are truly realized in forthcoming commercial SIMS instruments, this will establish SIMS as the pre-eminent surface analytical technique.

A truly small spot SIMS (ca. 50nm) would allow the investigation of surface films and coatings on individual fibers in virtually any matrix. While the complex mass spectra generated by SIMS can be difficult to quantitate, the use of standards would be expected to mitigate that difficulty as well as the identification of mass fragments for chemical identification of surface constituents.

At this point, however, the single most useful analytical technique for the examination of composite interfaces is transmission electron microscopy. As with most microanalytical techniques, the preparation of the sample is critical, both with respect to the production of a specimen which is electron transparent in the regions of interest and to the minimization of artifacts caused by sample preparation (see for example¹⁴). While some thin sections are made via ultramicrotomy, the predominant mode of ceramic composite thin section production is via ion milling techniques. In order to ion mill a sample, the selected region of interest must first be mechanically thinned using some combination of techniques. The pre-thinned sample is then bombarded with one or more ion beams in much the same manner as a dirty building is cleaned with sand blasting equipment. Upon thinning to penetration, the milling is ceased and regions of electron transparency are sought out and selected. The preparation of "good" thin sections is an art capped by repetition, good luck and the recognition of artifacts such as preferential sputtering.

An excellent example of area selection and subsequent thin film formation is shown in a paper by Ruhle et al.¹⁵ wherein they were interested in examining a crack front. The sample was back thinned after the area of interest was selected in order to preserve the character of the area of interest. Careful sample preparation in this example made it possible for them to confirm that crack bridging by whiskers is necessarily accompanied by some interfacial debonding.

The first line of TEM sample examination is standard bright field (BF) examination wherein the beam of electrons forms a projected image in a manner qualitatively similar to that which a flashlight beam forms after penetrating a semi-transparent form of differing density. The resultant image is the result of a number of different imaging mechanisms (electron

transmission, channeling, diffraction and phase contrast, etc.) and may be interpreted in a standard manner.

Electrons passing through a crystalline material are diffracted and yield a spot pattern for a single crystal and a ring pattern for polycrystalline material. Deviations from these ideal patterns can be explained via structural models that predict streaking and double spots, etc. Selected area diffraction utilizes a set of blades or a small aperture to limit the region of electron transmission to an area of selected interest and thereby limits the diffraction information to that selected area. However, mechanical blades or apertures are limited to regions of no smaller than a few micrometers in diameter while regions of interest can often be considerably smaller than that.

Scanning transmission electron microscopes (STEMs) and TEMs with a spot capability are capable of focussing the electron beam down to a spot size of a few angstroms and thereby selecting a spot or very small region from which to collect a diffraction pattern. This technique is called micro or micro-micro diffraction. From the spacings of the spots and/or rings in a diffraction pattern, it is often possible to identify a crystalline phase (much as in XRD) and often a crystal orientation as well.

In order to complement the electron diffraction analysis, the analytical techniques of energy dispersive x-ray spectroscopy and electron energy loss spectroscopy (EELS) can be used. The first technique is the same as that commonly used with scanning electron microscopy and is complicated only by the very low currents used and small volumes of analysis. Although x-rays from a cubic micron or so may be generated and detected from samples in an SEM, the TEM samples are very thin and so both limit the analysis volume (and thereby the absolute number of emitted x-rays) and dramatically improve the spacial resolution of the technique. EELS uses an electron spectrometer to identify elements present in the sample by measuring the amount of energy lost in electrons which have been transmitted through the sample. This technique has traditionally been oriented toward the identification of light elements.

Despite the excellent resolving capabilities of the technique of transmission electron microscopy, the investigation of ultra-thin films (ca. tens of angstroms) can still present significant problems which

warrant the use of high resolution transmission electron microscopy (HREM) and specialized diffraction techniques. Clarke¹⁶ discusses the use of defocus, dark field, and lattice imaging to aid in the observation of thin intergranular films by electron microscopy.

By placing the objective aperture over the transmitted beam only, and imaging out-of-focus, the presence of an intergranular phase can be revealed by the formation of fringes originating at the boundaries between the grains and the intergranular phase where there is an abrupt discontinuity in the mean inner potential. This technique has the potential of demarking a thin film phase which is not readily resolvable in normally focussed bright field imaging.

Normal bright field imaging uses only the central transmitted beam to form an image. If, instead, the objective aperture is placed over a diffracted beam, then only the phase(s) responsible for that diffracted beam will be "illuminated". This is referred to as dark field (DF) imaging. If the intergranular film is amorphous or composed of extremely fine grains, then there will be a fuzzy ring associated with the diffraction pattern. If the objective aperture is placed over a portion of that ring to the exclusion of other diffraction rings and spots, the amorphous portion of the field of view will be preferentially illuminated.

When a crystal is properly oriented it is possible to take two (at least) beams passing through the objective aperture and form an image by the interference between these two beams. This image takes the form of a lattice corresponding to the resolvable lattice of the material being examined. Defects in the lattice thus formed may be interpreted as dislocations, twinning, etc. If an intergranular film is seen end on and the two adjacent grains are both in a strongly diffracting orientation, then high contrast lattice fringes can be imaged on both sides of the interface and critical examination may be made of crystallinity of the intergranular film.

When the intergranular film is not viewed head on, other diffraction techniques may be brought to bear to elucidate the relative crystalline orientation of the two lattices and the intergranular film. These techniques of analytical and high resolution transmission and scanning transmission electron microscopy make this an extremely powerful analytical

technique uniquely suited to the direct examination of ultra-small interfaces.

As Lewis and Rice¹ point out, the state of the fiber/matrix interface is probably not due to a single factor, but is dependent on a combination of factors including processing parameters; chemistry of the fiber/whisker, matrix and coating; chemistry of additives (e.g. sintering aids), and so forth. Moreover, there is more to be considered with the selection of a coating than direct mechanical properties. Fiber coatings can protect fibers from mechanical damage during handling and processing and can provide chemical protection from attack by the matrix during the processing¹⁷.

The initial state of the second phase is of significance and processing difference are capable of producing structural and/or chemical differences of significance even within the same material. Wet ground Si_3N_4 powders, for example¹³, have been shown to have much less surface oxidation than the same powders which have been dry ground. This initial oxidation film has been implicated in some work¹⁸ with SiC reinforced hot pressed Al_2O_3 and Si_3N_4 composites as the reason for embrittlement. It does not, however seem to really matter at what point the oxide films forms. Oxide films, in general, seem to form strong bonds which embrittle the composite and are to be avoided if possible. Thus it is to be expected that systems which form strong bonds are most amenable to the positive influence of coatings which mitigate that bonding¹⁷ while, for example, coatings have been of little benefit in ZrO_2 matrices which do not show strong interfacial bonding.

Most work on interfacial bonding in composites has been done on SiC whisker or fiber reinforced systems (for example,^{5,19,20}) from different sources (rice hulls, VLS, etc.) and although some work has been done linking void formation at the fiber interface²¹ with embrittlement, strong evidence exists that the formation of a thin, glassy amorphous region^{16,19,22,23} is responsible for embrittlement and may be independent of the matrix material and processing for Si_3N_4 and Al_2O_3 systems¹⁸. Nonetheless, a lack of amorphous interfacial region has been noted by several researchers in specific SiC reinforced systems^{19,24} which may be due either to conflicting interpretations or actual process differences.

It is fairly clear that a thin poorly bonding layer such as carbon⁵ or boron nitride¹² coating on fibers in room temperature composites will provide significant increases in toughness. Unfortunately, high temperature oxidation (600°C and up)^{19,25,26} is frequently cited as responsible for the oxidation of the interfacial region changing the carbon film into a silicate and the BN into a boron oxide. There is, however, some evidence that higher temperature oxidation may be less damaging^{1,5} as a diffusion barrier is set up which prevents the inward migration of oxygen and the outward migration of oxidation products. Some work has been done examining metal coatings such as silicon and boron¹² in the expectation that these would promote crack healing. While both may do this, it is clear that silicon bonds too strongly to the SiC fibers.

The techniques described above will be used to characterize the interface region for our whisker and fiber toughened silicon nitride materials. This characterization, along with mechanical property evaluation, will allow development of optimized processing conditions.

Computer Controlled Nitriding Furnace

In order to optimize the nitriding process for reaction sintered silicon nitride composites we are developing a computer controlled nitriding system. The main component of the facility is a rapid response, low mass, water cooled furnace with a maximum temperature capability of 2200°C in vacuum (1700°C in nitrogen). The furnace can be heated to maximum temperature in less than ten minutes. It can cool from maximum temperature in thirty minutes in a helium atmosphere and ninety minutes in vacuum. The heating element is tungsten mesh. The furnace hot zone is 104 mm in diameter (4 in.) and 203 mm in length (8 in.). The radiation shields and work support hearth are tungsten sheet. Temperature is monitored by two tungsten-5 rhenium, tungsten-26 rhenium thermocouples. Temperature can also be monitored optically through a shuttered viewing window located at the midpoint of the hot zone.

Major components of the power supply are a 480 V silicon controlled rectifier power regulator and a 34:1 step down transformer rated at 30 KVA. Power is distributed from the step-down transformer secondary to the

furnace by water cooled power leads. Water flow control switches for the cooling water supply to the power leads and furnace shell are interlocked to the power supply through a magnetic contactor. A water flow rate drop to less than normal level will trip the contactor, shutting off power to the furnace.

The furnace is equipped with a rotary mechanical vacuum pump and an oil diffusion pump and can maintain a vacuum level of 5.33×10^{-4} Pascal (4×10^{-6}) Torr at ambient temperature. A manual gas supply system with valves and two rotameters supplies gas at the viewing port or at a gas inlet port 180° from the window. A compound gauge allows monitoring of the pressure. We have supplemented this system by installing a MKS mass flow meter calibrated for 0-200 SCCM delivery. The output of this flow meter is 0 to 5 V DC proportional to gas flow. A vacuum rated solenoid valve is used to turn the gas supply on and off. Gas pressure is monitored by a Setra pressure transducer calibrated for 0 to 172 KPa (0-25 psia), producing a 0 to 5 V DC signal.

The control system for this furnace is shown schematically in Figure 1. The heart of the control system is a CamileTM 2000 data acquisition and control system (Dow Chemical Company, Midland, MI) interfaced with an AT type IBM PC compatible host computer. The PC compatible computer provides the user interface, while the Camile handles input from and output to the various facility components. The Camile unit is configured with an eight channel general purpose signal conditioning card which provides signal conditioning for the two thermocouple inputs from the furnace. It also contains an eight channel differential analog input card with 12 bit accuracy which accepts the 0 to 5 volt dc signals from the mass flow meter and the pressure transducer. A gravimetric module based on a low force load cell is being designed to monitor sample mass during the run.

An eight channel analog output card provides a 0 to 20 ma signal to the silicon controlled rectifier. This signal output is proportional to the input signal from the control thermocouple input to Camile and controls programmed temperature changes. The cards also provide a 9 V dc signal to operate a relay which controls opening and closing of the solenoid in the gas line. Opening and closing of the solenoid valve is controlled by the

Figure 1. Schematic of computer controlled nitriding furnace.

input signal from the pressure transducer according to the program entered in the host computer.

The Camile system provides complete software for operating each input and output device and for programming furnace operations. Control parameters driving the program are furnace temperature and pressure which are converted to moles of nitrogen consumed. This information will be used to adjust the furnace temperature and pressure according to a nitriding process model. This intelligent, real-time control will assure complete conversion of the matrix material while minimizing fiber degradation.

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GT-1(A) - MODELING OF FIBROUS PREFORMS
FOR CVD INFILTRATION

T. L. Starr

Energy and Materials Sciences Laboratory
Georgia Tech Research Institute
Atlanta, Georgia 30332

INTRODUCTION

Chemical vapor infiltration (CVI) has demonstrated considerable promise as a technique for fabrication of fiber reinforced ceramic composites. Unidirectional and bidirectional composites of SiC fibers in a SiC matrix have shown good strength and exceptional strain tolerance.

An analytical model provides insight into the CVI process, helps identify key processing parameters, and guides experimental process optimization efforts. The one-dimensional model developed for a random fiber preform has been modified to simulate the densification process with a cloth lay-up preform. Methods for extending the model to three-dimensions have been reviewed.

DISCUSSION OF CURRENT ACTIVITIES

Three-Dimensional Model

The one-dimensional model described in previous reports gives good agreement with experimental results obtained at ORNL for densification of disc-shaped preforms. One reason for this result is that the experimental arrangement is, in fact, effectively one-dimensional. Both heat and gas flow through the disc from one face to the other with only a small amount of radial flow. Embedded thermocouple measurements in the preform indicate an axial thermal gradient of 240 deg/cm but, radially, only 7 deg/cm at the cool face and 64 deg/cm at the hot face¹. Thus, the average heat flow in the radial direction is only about 10% of the axial flow. Experimental measurement of the gas flow within the preform has not been performed, but

the construction of the preform holder effectively constrains this flow to the axial direction. Future application of CVI technology certainly will utilize more complex shapes and flow patterns. Extension of the CVI model to three-dimensions is required to simulate the processing of these components.

Fundamentally, the CVI model is based on conservation equations for mass, energy and momentum. These differential equations express, in mathematical form, the physical requirement that the total mass, energy and momentum of a system is unchanged. Within a particular volume element, any change with time is equal to the difference between the flux in and the flux out. With densification times of several hours to several weeks, the spacial variations in CVI are much larger than the temporal variations. Thus, the steady-state approximation is appropriate, leading to a substantial simplification of the conservation equations.

The mass balance equation in the z-direction has the form:

$$-D_i \frac{d^2 X_i}{dz^2} + U \frac{dX_i}{dz} + R(X_i) = 0 \quad (1)$$

where D_i is the diffusion coefficient of the i th chemical species, X_i is its mass fraction, and $R(X_i)$ is its rate of formation or reaction. U is the velocity of the overall gas flow. A separate equation is needed for each important chemical species in the system and for each direction.

The energy balance equation has the form:

$$K \frac{d^2 T}{dz^2} + UC \frac{dT}{dz} + S = 0 \quad (2)$$

where K is the thermal conductivity, C is the heat capacity of the gas and S is related to the heat of reaction. For typical CVI processes the heat due to reaction and the heat flow due to gas convection are small relative to the conduction term.

The momentum balance equation has the general form:

$$\mu \frac{d^2 U}{dz^2} + \rho U \frac{dU}{dz} + \frac{dP}{dz} + \frac{\mu}{k} U = 0 \quad (3)$$

where μ is the gas viscosity, ρ is the gas density, P is the pressure and k is the preform permeability. For flow within the preform the first two terms are small and the momentum equation reduces to Darcy's law.

While several methods for solving these equations are known, the "finite volume" method² has proven effective and efficient for problems of linked mass and heat flow, including modeling of chemical vapor deposition (CVD) in a variety of reaction geometries^{3,4,5}. In this method the furnace and preform are modeled as a orthogonal array of volume elements. The differential equations are converted to a system of linear equations and solved numerically. Careful formulation of the coefficients in the linear equations assures that the solution matches physical reality, even at boundaries where abrupt changes in the properties occur.

This method can be applied to the ORNL forced CVI process. All of the experimental work with this process has utilized a disc or tube shaped preform. This geometry is modeled most effectively using cylindrical coordinates. Because of symmetry all of the angular terms in the conservation equations are zero and the problem becomes effectively two-dimensional in the axial and radial coordinates.

For forced flow CVI the inertial terms in the momentum balance equation are small and only the terms due to viscous flow within the porous preform are retained. The large surface area within the preform provides good heat transfer between the gas and the solid material, and these phases can be assumed to be in thermal equilibrium. With this assumption, the convection term in the energy balance equation is eliminated by including a convection component in the thermal conductivity parameter. For MTS deposition the heat of reaction term in the energy equation is small and also can be neglected. Finally, for stoichiometric SiC deposition the effective reaction rate can be expressed in terms of MTS concentration only, although intermediate reactive species are certainly involved.

Solution of these equations is relatively straightforward, given appropriate values for the coefficients and boundary values. Determination of some of these is still unresolved and, at this time, prevents complete

implementation of the model. The major uncertainties are in the values for the permeability coefficients and in setting the boundary conditions for the thermal model.

With the one-dimensional model the gas permeability is not needed for modeling the CVI deposition rate. The gas can flow only in one direction and the flow rate is held constant using mass flow controllers. Only the end point, the point at which the backpressure reaches the maximum allowable value, depends on the permeability. For a three-dimensional model the gas flow pattern is more complex, depending on the relative values of the permeability in each volume element. Accurate calculation of the deposition rate in each volume element depends on accurate calculation of this flow. Although estimation techniques for chopped fiber preforms were identified earlier in this program⁶, these are inadequate for cloth lay-up preforms. In this case, the permeability likely will be different in different directions relative to the fiber orientation. Experimental measurements of gas permeability for these materials is needed.

To some extent determination of the thermal conductivities faces the same uncertainties as described above for the permeability, although recent experimental measurements for cloth lay-up SiC/SiC composites do provide some data^{7,8}. However, another uncertainty arises in specifying the boundary conditions for the thermal problem. With the ORNL experimental arrangement the temperature is controlled at points on both ends of the preform in the axial direction and these provide well determined boundary conditions. In the radial direction no comparable controlled temperature region exists and the boundary conditions are not well determined. Additional temperature measurements in the radial direction are needed to accurately specify the thermal part of the modeling problem.

A three-dimensional model for the forced CVI process has been developed, although implementation is not complete. Additional experimental measurements are required to provide physical properties and boundary values. Given these the model will simulate the infiltration process for a variety of shapes and furnace configurations and assist in development of optimum process conditions.

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INEL-1(A) - NONDESTRUCTIVE EVALUATION OF ADVANCED
CERAMIC COMPOSITE MATERIALS

J. B. Walter and L. A. Lott

Idaho National Engineering Laboratory
EG&G Idaho, Inc.
P.O. Box 1625
Idaho Falls, ID 83415-2209

INTRODUCTION

The objective of this program is to evaluate and develop nondestructive evaluation (NDE) techniques for advanced ceramic composite materials. The capabilities of current state-of-the-art NDE techniques to reliably detect and characterize defects will be determined. New and/or improved techniques will be developed as the needs are identified.

A SiC-reinforced SiC matrix composite is the first material system being studied. The material is fabricated by infiltrating fibrous preform structures with vapors that deposit on the fiber surfaces to form the matrix of the composite. Techniques to detect and characterize porosity and individual voids, known to be produced in the material and decrease its strength, are being investigated first.

Previously, we showed that through-transmission measurements of the ultrasonic velocity and transmitted energy correlate with porosity in the SiC-reinforced SiC matrix material. Laser-generated ultrasound has been useful for inspecting samples which are thick or exceptionally porous because of the greater ultrasonic energy coupled directly into the sample with this technique. Area scans of the transmitted energy reveal variations in the porosity and seeded voids within a sample. Since area scans of the velocity do not show voids, voids can be distinguished from porosity variations. Although the wavelength of the ultrasound which penetrates the material limits the ability to size and resolve individual voids, smaller voids can be detected.

DISCUSSION OF CURRENT ACTIVITIES

Propagation of Ultrasound

Work this reporting period has focussed on developing a physical/mathematical model of the propagation of ultrasound through the material. Improved understanding of the process is required to extrapolate from measurements on a limited sample set to predict the ultrasonic behavior of similar samples. Such a model would relate the ultrasonic measurements to the porosity of the sample, predict the detection limits for voids, and provide guidance for developing single-sided inspection techniques.

In these materials, where the ultrasonic attenuation is large, multiple scattering can be very important. Monte Carlo computation techniques offer a means of attacking this problem. The physics of the problem is included in the calculation in a straightforward fashion. Each aspect of the model, such as the source of the ultrasonic pulse, the distribution of the scatterers, and the scattering cross section, is treated independently of the others. Initially each is included as a simple approximation, which can be improved upon as needed. In particular, for now, the attenuation is treated as arising by scattering from a uniform distribution of spherical scatterers embedded in an isotropic medium. Two parameters, the number and size of the scatterers, are adjusted to obtain qualitative agreement with the measurements.

The model achieves good qualitative results. The attenuation calculated from the early arriving pulse is seen in Figure 1 to increase both with frequency and porosity, and the slope does not change much with porosity. These features were also observed in experimental data reported previously.¹ The model also reproduces pulse broadening, as evidenced in Figure 2; both the calculated and measured A-scans are significantly broader than the incident 2.25-MHz broad band pulse. This broadening is not present in the model when the density of scatterers is small or when the scattering is frequency independent.

Figure 1. The modeled attenuation increases with both frequency and porosity.

Figure 2. The recorded and modeled outputs for through-transmission with 2.25 MHz broadband piezoelectric transducers are significantly broadened by scattering from a high density of small scatterers.

These calculations assume that 20% of the porosity, by volume, is configured in pores which are 50% larger than the expected average pore size. This is reasonable, but we have been unable to obtain reliable measurements of actual pore size distributions. Corresponding calculations of the transmitted energy, in Figure 3, show that it falls off in a roughly logarithmic fashion with increasing porosity. Thus the logarithm of the transmitted energy varies approximately linearly with porosity for porosity changes less than several volume percent. The slope of the curve in Figure 3, calculated for the appropriate sample parameters, relates changes in the transmitted energy to differences in the porosity content.

The model works well for the early signal, which is used to calculate the transmitted energy and the attenuation. It permits differences in the transmitted energy to be related to differences in the porosity content of the samples, assuming sufficient samples are available to determine the pore size distribution. The model indicates that the logarithm of the transmitted energy varies approximately linearly with porosity for porosity changes of less than several volume percent.

Figure 3. Model predictions of the transmitted energy show that it falls off approximately logarithmically with increasing porosity.

Characterization of Fiber-Matrix Interface Bond

Work has begun on nondestructive techniques for characterizing the bond at the interface between the fiber and matrix in the composite material. The stresses at the fiber/matrix interface are known to influence the mechanical properties. The optimum material strength and fracture toughness are achieved at intermediate values of interface bond strength for which the mechanical load is transferred to the fibers while allowing significant fiber pullout to prevent brittle fracture.² A means of nondestructively characterizing the interface would potentially be valuable as a process development tool and as an NDE method for determining material toughness.

A review of the literature has revealed that dynamic mechanical techniques such as vibration response-internal damping measurements have yielded information on fiber/matrix interface properties and the presence of damage in polymer composites.^{3,4} Noncontacting laser vibration detection methods, with which INEL has had success in adhesive bonding studies,⁵ will be used with these composites.

Acoustic emission measurements will be performed during the application of bending stresses to study behavior of the fiber/matrix interface and material damage such as fiber breakage and matrix cracking. Experimental equipment has been assembled and preliminary experiments begun. Results of the experiments will be reported for the next period.

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INEL-1(B) - JOINING OF SILICON CARBIDE REINFORCED CERAMICS

Dennis N. Coon and Robert M. Neilson, Jr.

Idaho National Engineering Laboratory
EG&G Idaho, Inc.
P.O. Box 1625
Idaho Falls, ID 83415-2218

INTRODUCTION

Recent advances in polymer and metal matrix composites have elevated them to the status of practical engineering materials. These advances have also prompted intensive research efforts to develop advanced ceramic fiber/ceramic matrix composites for high temperature applications. To fully realize their potential, reliable and practical joining techniques must be developed that will permit the use of ceramic/ceramic composites as complex or integrated components in engineering designs. Such joints require sufficient strength and toughness for the projected application as well as resistance to environments and thermal degradation characteristics comparable to those of the composite joined.

This research program will identify and develop techniques for joining silicon carbide fiber-reinforced ceramic composites of tubular geometries, primarily through the use of glass joining materials. The general tasks of this program include identifying, preparing, and characterizing compositions suitable for joining ceramic/ceramic composites; developing a joining methodology and evaluating the effects of process parameters on joint characteristics; fabricating and characterizing joints; and determining physical/mechanical properties and failure behavior of joints under ambient conditions, elevated temperatures, and simulated service environments.

DISCUSSION OF CURRENT ACTIVITIES

The research effort during the past six months has been concentrated on (1) determining the effect of Nb_2O_5 additions on the reactivity of an $\text{MgO-Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glass with SiC in air and nitrogen atmospheres,

- (2) development of a joining geometry amenable to shear testing, and
 (3) determining the effect of Nb_2O_5 additions and atmosphere on joint strength and morphology.

Effect of Nb_2O_5 Additions on Reactivity of Glass and SiC

The effect of Nb_2O_5 additions to glass composition 7a-T on the reactivity between SiC and the glass was examined. Mixtures of approximately 10 wt% SiC powder and 90 wt% glass powder were prepared from glass compositions 7a-T, 7a-T + 2-1/2 Nb, and 7a-T + 5 Nb. The glass compositions, given in Table 1, represent additions of 0, 2.5, and 5.0% Nb_2O_5 , respectively, to glass composition 7a-T. The glass-SiC mixtures were placed in platinum boats and heat treated in either air or flowing nitrogen. The sample size was approximately 200 mg, and the sample weight was monitored as a function of time at temperature.

TABLE 1. GLASS COMPOSITIONS USED IN THIS STUDY

Glass	Composition (wt%)					
	SiO_2	Al_2O_3	Li_2O	MgO	TiO_2	Nb_2O_5
7a-T	61.8	14.4	8.6	12.3	2.8	--
7a-T + 1/2% Nb_2O_5	61.5	14.3	8.6	12.2	2.8	0.5
7a-T + 2-1/2% Nb_2O_5	60.3	14.0	8.4	12.0	2.7	2.5
7a-T + 5% Nb_2O_5	58.7	13.7	8.2	11.7	2.7	5.0

Two reactions which result in weight changes have been reported.¹
 First is oxidation with the formation of a solid product:

The SiO_2 reaction product would be expected to form at the SiC/atmosphere interface. Without a molten glass present, the SiO_2 layer would be stable, and oxidation would proceed by diffusion of oxygen

through the SiO_2 layer. In the presence of a molten glass which is not saturated with SiO_2 , the product layer would be expected to dissolve and expose fresh SiC surface for continued oxidation. Since diffusion through SiO_2 has been reported to be slower than the surface reaction,¹ the presence of a molten glass is expected to enhance oxidation.

The weight change per mole of SiC oxidized (ΔW_m) can be expressed as:

$$\Delta W_m + Q_{\text{SiO}_2} - Q_{\text{SiC}} = 20 \text{ g} \quad (2)$$

where the molecular weights of SiO_2 and SiC are expressed as Q_{SiO_2} and Q_{SiC} , respectively. The number of moles of SiC oxidized (ΔM_{SiC}) during heat treatment can then be expressed by:

$$\Delta M_{\text{SiC}} = \Delta W + \Delta W_m \quad (3)$$

$$= \Delta W + 20 \quad (4)$$

where ΔW is the observed weight of the powder mixture. The number of moles of SiC ($M_{\text{SiC}})_o$ in the original sample can be expressed as:

$$(M_{\text{SiC}})_o = (W_{\text{SiC}})_o + 40 \quad (5)$$

where the weight of SiC in the sample is given by $(W_{\text{SiC}})_o$. Therefore, the fraction of SiC oxidized, on a mole basis f_{SiC} , is given as:

$$f_{\text{SiC}} = \frac{\Delta M_{\text{SiC}}}{(M_{\text{SiC}})_o} \quad (6)$$

Combining Equations 4, 5, and 6:

$$f_{\text{SiC}} = 2 \frac{\Delta W}{(W_{\text{SiC}})_o} \quad (7)$$

Equation 7 provides a simple relationship to monitor the amount of SiC oxidized, and a weight increase would be expected.

A second possible reaction has been proposed to occur in reducing environments¹ that results in gaseous products:

In this instance, the weight change is a negative 40 grams per mole of SiC oxidized. Following the same procedures as previously outlined:

$$f_{\text{SiC}} = \frac{\Delta W}{(W_{\text{SiC}})_0} \quad (9)$$

In this instance, the weight change expected is a weight loss.

Figures 1, 2, and 3 show the amount of SiC oxidized in glass/SiC mixtures with time and temperature for glass compositions 7a-T, 7a-T + 2-1/2% Nb₂O₅, and 7a-T + 5% Nb₂O₅. The mixture comprised of 90% glass 7a-T and 10% SiC exhibited rapid oxidation and near complete conversion of the SiC to SiO₂ in 10 min at 1050°C, Figure 1. However, as the temperature was increased, the fraction of SiC oxidized decreased for a constant time. One would predict that oxidation should occur more rapidly at higher temperatures, therefore, it can be hypothesized that a second reaction mechanism becomes operable at higher temperatures. The nature of that mechanism is not understood to date. However, all samples were observed to gain weight with time at temperature.

Figure 2 shows the effect of heat treatment time and temperature on the fraction of SiC oxidized for a mixture of 10% SiC with glass 7a-T + 2-1/2% Nb₂O₅. In this instance, each sample gained weight with time at temperature. However, the temperature trends are not as clear. A heat treatment temperature of 1050°C resulted in the largest fraction of SiC oxidized. There appeared to be little difference in the samples heat treated at 1125, 1200, and 1275°C, although the sample heat treated at 1125°C exhibited the smallest fraction of SiC oxidized. Similar temperature trends were observed for the mixture of 10% SiC with glass 7a-T + 5% Nb₂O₅, Figure 3. Again, the sample heat treatment at 1125°C exhibited the smallest fraction of SiC oxidized. However, as the heat treatment was increased to 1275°C, the fraction of SiC

Figure 1. Fraction of SiC oxidized in a glass/SiC mixture for glass 7a-T.

Figure 2. Fraction of SiC oxidized in a glass/SiC mixture for glass 7a-T + 2 1/2% Nb₂O₅.

Figure 3. Fraction of SiC oxidized in a glass/SiC mixture for glass 7a-T + 5% Nb₂O₅.

oxidized appeared to increase with increasing temperature. Also, all samples exhibited a weight increase with increased time at temperature for all temperatures investigated.

The effect of Nb₂O₅ content on the fraction of SiC oxidized is shown in Figures 4, 5, 6, and 7. No effect was observed at a heat treatment temperature of 1050°C, Figure 4. At a heat treatment temperature of 1125°C, no clear trends with Nb₂O₅ content are observed, Figure 5. Also plotted in Figure 5 are weight change data obtained in a flowing nitrogen environment. As expected, very little SiC was oxidized in the nitrogen environment; however, the addition of 5% Nb₂O₅ did decrease the amount of SiC oxidized. It is presumed that oxidation was caused by a small amount of oxygen in the system at the time of the test. Figures 6 and 7, for 1200 and 1275°C, show that the fraction of SiC oxidized increased with increasing Nb₂O₅ content. It is clear that Nb₂O₅ additions promote oxidation of SiC in air at these higher temperatures.

X-ray diffraction analysis was used to examine heat treated samples for the presence of niobium carbide. No niobium carbide was detected in any sample heat treated in air. However, niobium carbide was detected in samples heat treated in nitrogen, as well as LiAlSi₂O₆, Mg₂SiO₄, and SiC. Niobium carbide was detected in the samples in which Nb₂O₅

Figure 4. The fraction of SiC oxidized in a glass/SiC mixture as a function of Nb_2O_5 content for glass 7a-T at 1050°C.

Figure 5. The fraction of SiC oxidized in a glass/SiC mixture as a function of Nb_2O_5 content for glass 7a-T at 1125°C showing results obtained in air and N_2 .

Figure 6. The fraction of SiC oxidized in a glass/SiC mixture as a function of Nb_2O_5 content for glass 7a-T at 1200°C showing results obtained in air and N_2 .

Figure 7. The fraction of SiC oxidized in a glass/SiC mixture as a function of Nb_2O_5 content for glass 7a-T at 1275°C showing results obtained in air and N_2 .

was present in the glass. The phase identified was NbC and the positions of the three major peaks are noted in Figure 8. Notice that the intensity of the NbC peaks increased with increased concentrations of Nb₂O₅.

Samples were prepared for mechanical testing to determine the effect of Nb₂O₅ additions, and NbC formation, on the mechanical behavior of joined composites. It was reported² that joined specimens tested in flexure always failed along the glass/composite interface. While coverage of the joining glass on the composite was good, low flexural strengths resulted from a weak glass/composite interface. As a result of those earlier tests, a shear test geometry was used, Figure 9. The joints prepared in this geometry covered an area approximately 22 x 6 mm and were typically 75 x 10⁻³ mm thick. The mechanical test consisted of a simple "push-off" test and the load, P, required for catastrophic failure was determined. The shear strength was calculated from the failure load and joint area.

The shear strength results are reported in Table 2. The shear strength was typically a factor of 5 to 10 lower than the flexure strengths previously reported for samples prepared under similar conditions. For samples prepared in air, longer joining times reduced the shear strength from 3.8 to 0.5 MPa. This result is consistent with flexural strength tests.²

TABLE 2. EFFECT OF Nb₂O₅ ADDITIONS ON MECHANICAL STRENGTH-SHEAR GEOMETRY

<u>Glass Composition</u>	<u>Joining Atmosphere</u>	<u>Joining Temperature (°C)</u>	<u>Joining Time (min)</u>	<u>Strength (MPa)</u>
7a-T + 1/2% Nb ₂ O ₅	Air	1125	10	0.5
7a-T + 1/2% Nb ₂ O ₅	Air	1125	5	3.8
7a-T	Nitrogen	1125	30	4
7a-T + 5% Nb ₂ O ₅	Nitrogen	1125	30	7

Figure 8. X-ray diffraction results for samples containing 0, 2.5 and 5.0% Nb_2O_5 heat treated at 1125°C in N_2 .

A micrograph of the fracture surface prepared in air at 1125°C for 10 min is shown in Figure 10a. The coverage of glass on the surface is poor, and the limited chemical interaction between the glass and composite resulted in a weak interface. Figure 10b shows the fracture surface of a specimen prepared with glass 7a-T in nitrogen at 1125°C for 30 min. Based on the results of samples prepared in air, the longer joining time would be expected to degrade the shear strength. The shear strength was 4 MPa, slightly higher than that of samples prepared in air, and the coverage of glass on the surface was improved. However, there was very little chemical interaction between the glass and composite. The fracture surface of a specimen prepared with glass 7a-T + 5% Nb₂O₅ in nitrogen at 1125°C for 30 min is shown in Figure 10c. The coverage of glass on the surface was excellent and chemical interaction between the glass and composite resulted in "pull-outs" on the fracture surface. Presumably, the chemical interaction and improved interface strength resulted from the formation of niobium carbide as discussed elsewhere in this report.

Conclusions

The ability to join SiC fiber reinforced/SiC matrix composites with a MgO-Li₂O-Al₂O₃-SiO₂ glass has been demonstrated. It is necessary to add Nb₂O₅ to the glass and prepare the specimen in nitrogen to provide excellent coverage of the glass on the composite surface and a chemical interaction between the glass and SiC. NbC, identified by x-ray diffraction, results from the reaction of Nb₂O₅ in the glass with the SiC composite.

Future Direction

The stability of NbC, formed during joining, upon reheating in both air and nitrogen environments will be studied. Optimum process variables for the formation of NbC will be determined. Two directions to limit the extent of oxidation will be pursued. First, the use of more refractory glass compositions and of joining heat treatments based on simultaneous sintering and crystallization of a glass powder³ will be examined. The intent is to

Figure 8. (Continued)

Figure 9. Shear test geometry used for measuring the failure strength of joints.

A micrograph of the fracture surface prepared in air at 1125°C for 10 min is shown in Figure 10a. The coverage of glass on the surface is poor, and the limited chemical interaction between the glass and composite resulted in a weak interface. Figure 10b shows the fracture surface of a specimen prepared with glass 7a-T in nitrogen at 1125°C for 30 min. Based on the results of samples prepared in air, the longer joining time would be expected to degrade the shear strength. The shear strength was 4 MPa, slightly higher than that of samples prepared in air, and the coverage of glass on the surface was improved. However, there was very little chemical interaction between the glass and composite. The fracture surface of a specimen prepared with glass 7a-T + 5% Nb₂O₅ in nitrogen at 1125°C for 30 min is shown in Figure 10c. The coverage of glass on the surface was excellent and chemical interaction between the glass and composite resulted in "pull-outs" on the fracture surface. Presumably, the chemical interaction and improved interface strength resulted from the formation of niobium carbide as discussed elsewhere in this report.

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(a)

(b)

(c)

Figure 10. Fracture surfaces for joints prepared at 1125°C: (a) glass 7a-T in air for 10 min, (b) glass 7a-T in N_2 for 30 min, (c) glass 7a-T + 5% Nb_2O_5 in N_2 for 30 min.

increase the viscosity of the glass at the joining temperature and increase the SiO_2 in the glass to limit dissolution of the oxide formed at the SiC surface. The second approach to limit oxidation is based on the highly exothermic reactions between SiO_2 and "reactive" metals (i.e., Al, Mg, Zr, and Y) in the presence of carbon. The product is SiC and metal oxides. This series of reactions may provide a nonvitreous joining technique. The vitreous and nonvitreous joining techniques would be complementary and provide a much broader range of applications in which this joining technology could be used.

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INEL-1(C) - SUPERCONDUCTING FILM FABRICATION RESEARCH

J. C. Debsikdar and E. G. Samsel

Idaho National Engineering Laboratory
 EG&G Idaho, Inc.
 P.O. Box 1625
 Idaho Falls, ID 83415-2218

INTRODUCTION

This program is investigating techniques for fabricating sol-gel derived films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ based superconducting ceramics with the ultimate goal of developing a fabrication technology that can produce useful devices. The sol-gel approach being investigated in this program involves controlled interactions of the alkoxide precursors of Y_2O_3 , BaO , and CuO . Suitable barium alkoxide is available from commercial sources. However, suitable alkoxide precursors of CuO are not commercially available. Commercially available yttrium alkoxides are extremely moisture sensitive and, consequently, difficult to hydrolyze in a controlled manner. Therefore, one of the tasks of this program is to develop method(s) of synthesizing alkoxy compounds of copper and yttrium for sol-gel synthesis and fabrication of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting films. The general tasks of this program include synthesis of alkoxide precursors; development of sol preparation procedure(s); preparation of sol-gel derived powders; film fabrication using sol as well as sol-gel derived powder slurry; and characterization of films in terms of superconducting properties, microstructure, and chemical homogeneity.

Previous work^{1,2} was done on (1) synthesis of two copper alkoxy complexes, namely, copper amyloxy acetylacetonate ($\text{C}_5\text{H}_7\text{O}_2\text{-Cu-OC}_5\text{H}_{11}$) and copper methoxyethoxyethanolate ($\text{O}_2\text{H}_{11}\text{C}_5\text{O-Cu-OC}_5\text{H}_{11}\text{O}_2$); and three yttrium alkoxy complexes, namely, yttrium triamyloxide [$\text{Y-(OC}_5\text{H}_{11})_3$], yttrium methoxyethoxyethanolate [$\text{Y-(OC}_5\text{H}_{11}\text{O}_2)_3$], and yttrium monochlorodiamyloxide [$\text{Y-(OC}_5\text{H}_{11})_2\text{Cl}$]; and (2) synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and chlorine substituted $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors, both of which showed critical temperature, T_c , of ~ 90 K. Moreover, it was

demonstrated that the sol-gel derived $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor was more homogeneous than that produced by conventional methods (i.e., solid state reactions of oxides and carbonates).

DISCUSSION OF CURRENT ACTIVITIES

Efforts during the preceding six months concentrated on (1) optimization of procedures for synthesizing copper and yttrium alkoxy complexes, (2) development of sol-gel techniques for producing both thin and thick $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting films, and (3) evaluation of coating microstructure.

Synthesis of Copper and Yttrium Alkoxides

In the preceding report,¹ the methods of synthesis of soluble methoxyethoxyethanolate complexes were reported. Further synthesis effort was directed towards process optimization. As reported earlier, the reactions of sodium methoxyethoxyethanolate and copper (II) chloride produced an insoluble by-product of unknown composition, thus the yield of soluble copper bisalkoxide by this route was low. Moreover, the reaction products, copper bisalkoxide plus insoluble by-product, are very viscous, making filtration difficult and time consuming. Therefore, our synthesis effort in this reporting period was directed towards development of an alternative route to minimize those problems. The current effort has resulted in the development of an improved chemical route which does not produce any insoluble by-product. The newly developed route may be schematically represented as follows:

Copper isopropoxide produced in Reaction (1) was washed free from LiCl in a dry-argon atmosphere using tetrahydrofuran (THF) because LiCl has appreciable solubility in THF. The washing step was assumed to be complete when the filtrate did not produce a silver chloride precipitate when reacted with silver nitrate solution. Reaction (2) was carried out under vacuum in order to remove isopropanol from the reaction product as soon as it is formed. As Reaction (2) proceeds, copper methoxyethoxyethanolate precipitates out, presumably because of its very low solubility in methoxyethoxyethanol. However, the material dissolves in THF.

We synthesized yttrium methoxyethoxyethanolate as shown in Reaction (3).

The solution of $\text{Y}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ in THF was purified by passing it through silica gel in an airless column chromatograph.

Film Deposition

Two approaches were taken for fabricating $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting films. These are (1) coating from sol for producing thin and thick films, and (2) coating from sol-gel derived powder-slurry for producing thick films.

Coating from Sol

The sol preparation procedure is schematically shown below.

Hydrolysis of the mixed alkoxy complexes was carried out with 1 mole water per mole mixed alkoxides. The concentration of the sol, as determined by a gravimetric method after hydrolyzing and calcination of the hydrolyzed product at 900°C for 2 h, was 4.6 g oxide/100 mL. The viscosity of the sol at room temperature, as determined by Cannon-Ubbelohde Semi-Micro viscometer, in dry-argon atmosphere was ~1.35 centistokes. The sol of the above characteristics was used to coat alumina substrates by spin coating at ~3000 rpm.

It may be mentioned here that the mixed alkoxide solution used for this coating work can be concentrated to produce a highly viscous and homogeneous paste-like fluid. We believe that the paste-like material could be used as a potential precursor material for producing fiber/wire by spinning and/or by extrusion process(es).

Coating from Powder-Slurry

The procedure for producing powder-slurry is schematically shown below.

For preparing the slurry, the mixture of alkoxides was hydrolyzed with 2 moles water per mole alkoxide to produce the gel. The gel was vacuum dried at -100°C, ground in an agate mortar, and then ultrasonically dispersed in isopropanol. The slurry coating was deposited on alumina substrates using a plastic eye-dropper.

Heat Treatment of Coated Substrate

Both sol and slurry coated substrates were heat treated at 990°C/1 h in a tube furnace in free-flowing oxygen (flow rate: 300 mL/min). This heat treatment schedule was chosen following the work of Michael Gross, et al.³ of AT&T Bell Laboratory.

Characterization of Sol and Slurry Derived Films

During this reporting period, the films were characterized for film thickness and microstructure by scanning electron microscopy (SEM). For thickness measurements, SEM photomicrographs were taken of the fractured edges of the specimens without polishing because polished specimens in epoxy showed a large number of fine particulate materials all over the coating/epoxy interface making it difficult to obtain satisfactory photomicrographs. Figure 1a shows the thickness of the sol-derived thin (~0.25 μm); Figure 1b shows the uncoated edge of the substrate at the

Figure 1. SEM photomicrographs showing (a) the thickness of sol-derived thin film and (b) the uncoated edge of the substrate.

same magnification for comparison. The apparent roughness of the film cross section (Figure 2) is due to the fact that this is a fracture surface. The coating/substrate interface is sharp and replicates the surface of the substrate. The thickness of the slurry-derived thick film (Figure 2) was $\sim 8 \mu\text{m}$, with a sharp coating/substrate interface.

Figure 2. SEM photomicrographs showing the thickness of slurry-derived thick film.

As shown in Figure 3, the microstructure of the sol-derived thin film was highly uniform and consisted of submicron size spherical particles. No cracks were observed in the film at this magnification. Another interesting feature of the microstructure is the absence of sharp grain boundaries. This is significant because the absence of grain boundaries in the film would be expected to contribute to increased critical current density. The microstructure of the slurry-derived thick film (Figure 3c and d), on the other hand, was coarse and consisted of plate-like grains of various sizes with sharp grain boundaries. Another characteristic feature of this film was the presence of intragranular microcracks.

Figure 3. SEM microstructure of sol-derived thin film [(a) and (b)] and slurry-derived thick film [(c) and (d)].

Whether or not these microcracks relate to the size of the grains⁴ and/or orientation or shape of the grains, or result from thermal stress during cooling is not clear at present.

The superconducting properties of both thin and thick films (namely, critical temperature, T_c , and critical current density, J_c) will be reported in the next semiannual report. Since the microstructural features of the sol-derived thin film showed greater promise than those of the slurry-derived thick film in terms of successful development of increased critical current density superconductors, our future research effort will be primarily directed to investigating techniques for fabrication of sol-derived films.

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LANL-1 - SHORT FIBER REINFORCED STRUCTURAL CERAMICS

P. D. Shalek and W. J. Parkinson

Los Alamos National Laboratory
Los Alamos, NM 87545

INTRODUCTION*

Structural ceramic materials are of particular interest to the Fossil Energy Materials Program. Applications for which these materials can be considered include high temperature heat exchanger systems, coal gasification hardware, and engine components. A prominent characteristic of ceramics which must be addressed for these applications is brittle fracture. Strength is limited by the size of pre-existing flaws and the fracture toughness, which is typically low in ceramics. Fracture is catastrophic and unpredictable. Short whiskers have been used to toughen these materials and important increases in fracture toughness and sometimes strength have been achieved. However, fracture remains catastrophic. This program addresses the need to improve the fracture toughness and the brittle nature of fracture to achieve both high and reliable strength characteristics, and graceful failure. The latter implies the existence of residual load-carrying capability after initial failure. Our approach is to extend the vapor-liquid-solid (VLS) process used to grow short SiC whiskers to the growth of long whiskers (up to 100 mm) and develop the use of these whiskers as semi-continuous, oriented reinforcement for ceramic matrices.

Two principal tasks are included in this work. One is to modify and optimize the existing VLS whisker growth process to produce long SiC whiskers. As part of this task, the groundwork will be established to incorporate an artificial intelligence (AI) system in the whisker growth process. An AI system offers the potential for markedly

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improving the yield, quality, and reproducibility of a product at a fraction of the human resources. Such a payoff is especially attractive from the standpoint of technology transfer. The use of the long whiskers will require some reassessment and modification of the harvesting and beneficiation procedures used for short whiskers. The second task entails the development of a staple whisker yarn. To help predict the performance of the yarn in composites, work will continue in characterizing the strength of long VLS SiC whiskers as a function of temperature and surface treatment.

DISCUSSION OF CURRENT ACTIVITIES

Whisker Growth and Processing

Growth Apparatus

Although VLS SiC whiskers of up to 2 1/2 inches in length were grown by modifying the standard reactor configuration, the techniques developed for making staple yarns ultimately reduced them in length to 1/2 inch or less. We thus reverted to using the standard setup, which was developed to grow whiskers of up to 3/4 inch in length for chopping, and using those as-grown lengths as staple fibers. We did not start up a production reactor during this period as planned, but did manage to build up a moderate inventory of whiskers for the textile development activities. Our production was held down by an inadvertent change in the quality of our furnace fused quartz muffle tubes which eventually resulted in our having only one tube in which to conduct whisker growth. This tube was then relegated to development work. The problem arose when the manufacturer switched to a more pure SiO₂ raw material, causing the tubes to deform at the temperature of 1400°C because of much less devitrification product. The manufacturer has since gone back to using the original raw material.

The new stable reactor design described in the last progress report¹ was extensively evaluated during this period and was found to give uniform growth of prime whiskers throughout the reactor with run-

to-run reproducibility when all of the other parameters were held as constant as possible. This design features a thin, replaceable porous-graphite floor plate which, in conjunction with the jets in the underlying reactor plenum, allows us to maintain the combined jet action/volume diffusion process-gas mixing which is essential for good growth in this particular reactor. The only problem, but an important one, encountered with this design was in assuring good contact between the floor plate and plenum surface for each run. This problem was solved by further design changes which are now being extended to a production reactor.

Process Variables

Plenum Pressure. In order to assure that the mixing conditions described above are consistently reproduced, the reactor plenum pressure is measured before each run for a standard gas flow with the floor plate in place.

Nucleation. With most of the important process variables believed to have been identified and under reasonable control, it was possible to confirm that whisker morphology is very sensitive to nucleation conditions. For the stainless steel (SS) flake catalyst, for example, progressively faster ramping to the growth temperature caused a progressive change from carbon- to silica-rich whisker growth. Under the same conditions where flake SS gave Si-rich growth, the same concentration of particulate SS catalyst gave stoichiometric (prime) whiskers.

Process Gas Monitoring. Throughout the development work on VLS whisker growth, it has been observed that, for a particular growth temperature profile, the whisker morphology and yield are very dependent on the C/Si ratio and the Si supersaturation of the reactant gases, respectively. We have had no satisfactory way to quantify these parameters until just recently, when we installed and put into operation a gas chromatograph to monitor the inlet and exit process gases as shown in Fig. 1. The type of information we have obtained is illustrated in Fig. 2. In conjunction with thermodynamic calculations and some other

tests, it has enabled us to identify the reactions given below as most likely for our process.

1. For SiO generation:

Reaction (3) is much more favorable thermodynamically than reaction (1). The CH_4 participating in that reaction is believed to that produced via reverse reaction (2) rather than that introduced in the process gas mixture (H_2 , N_2 , CO , CH_4).

2. For SiC formation:

Calculations show that the reaction of SiO with CH_4 to form SiC is thermodynamically much more favorable than reaction with either carbon (solid) or CO. In this case, the participating CH_4 is believed to be that introduced in the process gas mixture.

Looking at the gas chromatograph data in Fig. 2, the CH_4 is seen to begin reacting at a little over 1200°C and to become completely consumed by about 1300°C . Besides furnishing C reactant to the liquid droplets (eq. 6), the CH_4 is also used up in reacting SiO to Si (eqs. 4 and 5) and in converting any O_2 from an air leak to CO. Identification of an air leak, such as shown in Fig. 2, is extremely important in understanding the results of a run as it will reduce the amount of C reactant available for whisker growth. An air leak is identified by the presence of excess N_2 in the exit gas. Similarly, the amount of SiO generated can be derived from the amount of excess CO in the exit gases after that formed in the overall reduction of SiO_2 to Si(liq) and that from an air leak is subtracted. This increased understanding is being directed toward "fine tuning" of the process and eventual computer control.

Figure 1. Setup for alternate inlet/exit process gas sampling (standard analysis: H_2 , CO_2 , Ar/O_2 , N_2 , CH_4 , CO).

Figure 2. Gas chromatograph data for a whisker growth run.

Thermodynamic calculations have also shown that free carbon in the system can also affect the chemical equilibrium, depending on its availability. This strongly suggests that the reactor, which is presently constructed in its entirety from graphite, should, except for the feed gas plenum and floor plate, be constructed of a nonreactive material such as sintered polycrystalline silicon carbide.

Expert Control System for Process

As discussed in previous reports, we are building an expert control system for our whisker growth process. The project is divided into two phases. The goal of Phase 1 is to develop an expert consultant to help operators set up whisker production runs. It will be designed to answer questions such as "If I want predominately 4A and 5A (prime) whiskers, what should my operating conditions be?" This type of information will be available in a large rule-based knowledge base. These rules will be derived from the data in our database. The goal of Phase 2 is to develop an expert control system in which we use the knowledge from the consultant knowledge base. This system will be designed to answer questions such as "I want predominately 4A and 5A whiskers and there is an oxygen leak in the system. How can I adjust the operating conditions to salvage the run?"

Even though we are continually learning more about the physics of the growth process, we do not understand it well enough to describe it accurately with a mathematical model. Since we aren't able to model the process, in order to run it or answer questions like those discussed above, we must rely on experts (people who have experience running the process). They observe the symptoms and apply the correct adjustments based on their experience with the process. This is an adequate approach as long as the experienced whisker expert is always available. But if we plan to transfer this technology to industry without transferring the experts as well, the most efficient thing to do is build an expert system to take the place of the experts. Phase 1 is designed to deal with the fundamental process and should be 100% usable by the recipient. Phase 2 will be designed specifically for our growth

process and may be slightly less useful to the recipient if their process is slightly different from ours. For this reason, it is important that Phases 1 and 2 be written so that they can stand alone if need be.

One of the most difficult aspects of building expert systems is capturing the knowledge of the expert. For various reasons, it is often hard for the expert to translate all his expertise, based on his many experimental observations, into the rule form we are requiring for our expert system. We are therefore using a database that will record all of our experimental observations. We will analyze the information in this database to learn, for example, "When A happened, the expert did B and the results were C."

We have again rebuilt and restructured our database. Now that we are getting such good data, our philosophy is to take and store as much data as possible from each run. In a relational database management system like INGRESS, which we are using, large amounts of data may be manipulated quite easily. We can query the database for information about any combination of data we have stored. This allows us to ask questions that were not anticipated when we structured the database.

The following data will be stored in the main run tables in the database:

1. The type of reactor and the number of times it has been used.
2. The type of growth plates and the number of times they have been used.
3. The number of times the overlay plate has been used.
4. The type of catalyst and the amount used.
5. The generator weight and weight loss.
6. The type of nucleation/growth cycle used.
7. The inlet and exit gas composition as a function of time.
8. The gas flow rate and pressure drop through the reactor.
9. The whisker yield, by whisker type and total yield.
10. The amount of SiO_2 generated.
11. The gaseous C/Si ratio in the reactor as a function of time.

Additional information, such as reactor dimensions, will also be stored in supplemental tables in the database. The table containing the characteristics of the nucleation/growth cycle will have time-temperature curves with slopes and magnitudes at various points. Some of the data will be direct experimental measurements and others will be calculated from the experimental results. We also intend to use the results of the chemical equilibrium code SOLGAS to compare the experimental results with the theoretically predicted results. But SOLGAS must first be modified, so these results won't be ready immediately. SOLGAS will be used in conjunction with the database to calculate values as needed rather than storing them all.

By manipulating the data in the database, we can find trends in the data and develop the rules and confidence levels for those rules to use in our expert system. We are quite optimistic about this approach because early in this project we were able to observe useful trends even though the data we were working with was poor.

Staple Yarn/Cloth Development

The Los Alamos National Laboratory gratefully acknowledges the assistance of Woven Structures, a division of HITCO, and the International Center for Textile Research and Development at Texas Tech University in pursuing this work.

As mentioned earlier, the "long" whiskers used for this work were grown in our standard reactor to lengths ranging up to 3/4 inches. Air-harvested whiskers were found much more amenable to dispersion in glycerine, as required by the yarn process, than razor-harvested ones so are now used exclusively in this work. Although air harvesting eliminated most of the unwanted short whisker growth and debris otherwise collected from the surface of a growth plate, there still remained the problem of eliminating the catalyst balls from the harvested batch.

The textile work during this period refined and extended the work of the previous period from the production of uniaxially aligned whisker

ribbons to the further processing of these ribbons into a "spin/wrap" yarn. The first step in the ribbon-making process is to disperse the whiskers uniformly in glycerine. This was found to be accomplished most efficiently by drawing air bubbles up through a dilute whisker/glycerine mixture using a separatory funnel. The bubbles are created by evacuating above the mixture and regulated with the stopcock below. Dispersion is aided by fine bubbles which attach to the whiskers. Many of the catalyst balls are sheared from their whisker base by the bubbling action and collect at the bottom of the funnel where they can be drawn off through the stem.

To form a ribbon, the whisker-glycerine dispersion (slurry) is poured into a tapered reservoir and caused to cast onto a porous moving conveyor belt where a vacuum slot helps produce the alignment. The ribbon is washed with warm water to remove the glycerine.

This ribbon process was combined with a spin/wrap step, as shown schematically in Fig. 3, to produce a staple whisker yarn. Here, the ribbon is cast over a core thread, then proceeds into the spin/wrap device where it is twisted onto the core thread with a wrapper thread which holds the yarn assembly together. The glycerine is then washed off and a thin coating of latex deposited and dried onto the yarn to give it integral strength and flexibility for weaving, being later burned out. The whiskers in yarns made by this type of process are normally oriented at about 45° to the yarn axis. The desired axial orientation can be obtained by combining two yarns with a reverse twist as shown in Fig. 4.

Figure 5 shows a spool containing 10 meters of yarn that were made using a prototype apparatus. Ribbons were vacuum-cast by hand into 18 inch lengths which were then run continuously through the spin/wrap section with hand application of latex. A second generation device to do the whole operation continuously and automatically was constructed and is presently undergoing trials. The continuous operation and improved design of the new device will give a much more uniform and smaller diameter yarn than that shown in Fig. 5, which is about 1/16 inch in diameter.

Figure 3. Spin/wrap device for making staple whisker yarn.

An alternate process for making a staple whisker yarn was brought to the prototype stage. It incorporates an aerodynamic/friction pathway in the drafting and twisting phase of spinning. The end result is expected to be a sort of minimum twist roving with potentially improved whisker alignment and density.

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Figure 4. Spin/wrap yarns combined with reverse twist to give axial whisker orientation.

Figure 5. Early spin/wrap yarn made with prototype apparatus operating in an incremental mode.

**NIST-1 - STRUCTURAL RELIABILITY AND DAMAGE TOLERANCE OF CERAMIC
COMPOSITES FOR HIGH-TEMPERATURE APPLICATIONS**

E. R. Fuller, Jr., R. F. Krause, Jr., M. D. Vaudin, and T. R. Palamides

National Institute of Standards and Technology
Institute for Materials Science and Engineering
Ceramics Division
Gaithersburg, MD 20899

INTRODUCTION

The achievement of higher efficiency heat engines and heat recovery systems requires the availability of high-temperature, high-performance structural materials. Structural ceramics and, more recently, ceramic matrix composites have received particular attention for these applications due to their high strength and excellent resistance to corrosion, erosion and thermal shock. Even with these positive attributes, improved reliability and extended lifetime under service conditions are necessary for structural ceramics and ceramic composites to gain wide industrial acceptance. This reliability is only achieved with improved knowledge of in-service damage modes and failure mechanisms, and the processing knowledge to improve this performance by microstructural modifications. The inherent problems are mechanical and chemical in nature and are enhanced by the high temperatures, reactive environments, and extreme thermal gradients and thermal cycling, to which these materials are subjected.

With an objective of improved performance for heat engine/heat recovery applications, the NIST program addresses these problems through a determination and characterization of major toughening mechanisms in ceramic composites, examining both model crack-fiber systems and "real" composites. A key aspect of the program is a determination of the critical processing factors which influence microstructure and interfacial behavior in these materials, and which thereby influence these toughening mechanisms. The activities of the program are grouped under two major work areas, each designed to develop key data, associated test methods and companion predictive models. The status of these two work areas are detailed below.

DISCUSSION OF CURRENT ACTIVITIES

Crack-Fiber Interactions

Novel Technique for Characterizing Fiber Bridging in Ceramic Composites

Summary. A fracture mechanics specimen known as the double-cleavage drilled-compression (DCDC) specimen has been used to study crack-fiber interactions and toughening increments in a model composite system of SiC monofilaments in a borosilicate glass matrix. The toughening increments were measured from changes in applied stress intensity factor as a function of crack length and number of monofilament fibers. Both the fiber-matrix debond strength and the interfacial frictional shear resistance, which influence these toughening increments, were measured independently by a single fiber pull-out test and were correlated with the toughness increases measured by the DCDC specimen.

Background. Fiber-matrix interfacial properties and the way in which a fiber debonds control the failure mode of ceramic matrix composites. Under tensile loading conditions, these materials generally fail by one of two mechanisms^{1,2}: brittle fracture with no influence from the reinforcing fibers or fiber pull-out with either partial or general fiber bridging. When such a crack reaches a fiber, two possible situations can generally develop. The first is that the crack propagates directly through the fiber producing no modification in overall toughness. This results in a brittle failure, although there may be an increase in strength. The second is that upon impingement, the crack deflects along the fiber-matrix interface, bows around the fiber, and rejoins ahead of the fiber³. Subsequently, the fiber pulls out of the matrix, inhibiting the free separation of the crack surfaces. In some situations, this subsequent fiber bridging can be interrupted by fiber fracture, resulting in only partial bridging.

The principal physical properties that determine which behavior occurs are the debond strength and the frictional shear resistance of the fiber-matrix interface. These properties are determined both by the components of the composite, the matrix and the fiber, and by the processing conditions that combined these components. In the present studies, these

properties and the toughening increment that they impart to a crack are measured by a single fiber pull-out test and by a fracture mechanics tests, respectively. The fracture mechanics tests uses a specimen, known as the double-cleavage, drilled-compression specimen, into which SiC monofilaments have been introduced perpendicular to the prospective crack plane.

Experimental Procedure. Double-cleavage, drilled-compression (DCDC) specimens were fabricated by sandwiching SiC monofilaments [ACVO SCS-6 SiC] between borosilicate glass plates [Pyrex glass, #7740], which were either 3.2 mm or 1.6 mm thick. Using a combination of glass thicknesses, various numbers of fibers could be incorporated into the matrix as simple arrays without a significant change in billet geometry. The specimens were diffusion-bonded by heating in an atmosphere of helium under a slightly positive gas pressure. To ensure proper fiber alignment and specimen reproducibility the glass plates were placed in a graphite mold which had guide grooves for the fibers. To aid the diffusion-bonding process, a dead weight load was applied to the composite billet to provide a hot-pressing pressure of 1.2 MPa.

The general heating cycle consisted of bringing the specimen slowly up to 660°C, holding for 3.5 h, heating to 705°C, holding for a specified time (as discussed below), and furnace cooling to room temperature. The maximum processing temperature of 705°C is above the annealing temperature of borosilicate glass (565°C), but not above the softening point (820°C). This temperature was selected to minimize sufficiently devitrification of the glass and to maintain billet dimensions and shape, while still achieving adequate bonding between the plates. The hold time at 705°C was varied according to the number of fibers which were incorporated into the billet: 135 min for one fiber; 120 min for two fibers; and 90 min for three fibers. This varied and complex heating schedule was required to suppress devitrification on the diffusion-bonded interface. Devitrification was more of an issue when the thinner (1.6 mm) glass plates were used, possibly due to the additional free surface area needed per billet or to a different surface texture on the thinner plates.

This fabrication sequence resulted in a small billet, which could be sectioned into three DCDC specimens. Following sectioning, a hole was drilled into the center of each specimen, and the specimens were polished.

The hole was placed so that the monofilaments were located symmetrically about the hole with their axes perpendicular to that of the hole; thus, the plane of the mode I crack was perpendicular to the fiber axis.

The specimens were loaded in compression at a crosshead displacement rate of 0.05 mm/min, using a screw-driven mechanical testing machine with a 50 kN load cell. When properly loaded, two symmetric mode I cracks emanated from the top and bottom of the center hole. The cracks typically initiated at an applied stress of about 70 MPa and propagated unstably for a distance of approximately 1.25 to 2.5 hole radii. A unique feature of the DCDC specimen is that the stress intensity factor, K_I , decreases with crack length, c , following the initial crack pop-in. A consequence of this is that an increasing stress must be continually applied to advance the cracks. The crack speed is accordingly controlled by the stressing rate.

For a range of crack lengths, the applied compressive stress, σ_{app} , crack length, and stress intensity factor are related by:

$$(\sigma_{app}\sqrt{r})/K_{Ic} = g(c/r) = \alpha + \beta \cdot (c/r), \quad (1)$$

where r is the hole radius, $g(c/r)$ is a dimensionless geometric function, and α and β are geometric constants. In this range, a constant stressing rate extends the cracks at a constant speed. In addition, the stiffness of the DCDC specimen compared to that of typical load cells results in a constant stressing rate test when the crosshead is run at a constant displacement rate.

The dimensionless geometric function, $g(c/r)$, was experimentally determined for the present testing configuration from specimens which contain no fibers. These "blank" specimens were fabricated in a similar manner to the composite specimens. The range of crack lengths over which Eqn. (1) was calibrated was approximately $3 \cdot (c/r)$ to $18 \cdot (c/r)$. In this range the slope, β , was approximately the same for various specimens, but there was noticeable scatter in the intercept, α . This may result from specimen misalignment or frictional effects at the ends of the specimen. This vertical shift in the calibration line is not of great concern since data for the toughening increment from various fiber arrays were normalized to the value of K_{Ic} for glass measured on the same specimen. A linear

regression of the data for six calibration specimens gave a slope β of 0.17 and an average intercept value α of 1.75.

During testing, the positions of the crack tips were monitored by standard photography using a cross-polarized illumination system with quarter wave enhancement plates to increase field brightness. The strain contours associated with these cracks were symmetric about the center hole. The position of the crack tip was taken as the nodal point of the strain contours. The double cracks were approximately equal in length. The technique of cross-polarized illumination gives a good value for the average crack-tip position because the strain contours are an average of the entire crack front, which is slightly curved for this type of specimen⁴.

To evaluate effects of processing on both bond strength and subsequent frictional shear resistance of the fiber-matrix interface, an independent single fiber pull-out test was developed; a schematic of the test configuration is shown in Fig. 1. With this experimental design an embedded fiber could be pulled from the matrix of the DCDC specimen directly without the need for further specimen preparation. This avoided any undesirable contamination of the fiber-matrix interface, which could result, for example, from the specimen polishing required for a fiber push-in test.

Once a DCDC specimen was fully cracked, it was physically pulled apart by hand. What remained was a 6.0 mm fiber, half of which was protruding from the glass matrix. A small metal capillary tube was filled with epoxy and bonded to the 3.0 mm protruding segment. Bonding to the glass matrix was avoided with a separating sheet of thin plastic. The remaining part of the test jig consisted of high-strength stainless steel wire and swivels, which minimized the potential for misalignment. The samples were tested in tension at a crosshead displacement rate of 0.10 cm/min on a screw-driven mechanical testing machine with a 50 N load cell.

Results and Discussion. The change in applied stress intensity factor, K_I , as a crack propagated past a fiber array was monitored for linear fiber arrays of one, two, and three fibers. The results give the toughening increment, $\delta(K_I)$, for the bridging influence of that fiber array. Results for a single fiber are plotted in Fig. 2. The data for two specimens from the same billet were plotted in this figure. Although the data do not precisely superimpose, the reproducibility is reasonable.

Fig. 1. Schematic illustration of the single fiber pull-out test used to measure the debond strength and frictional shear resistance of the fiber-matrix interface from fibers protruding from half of a double-cleavage, drilled-compression specimen.

Fig. 2. Applied stress intensity factor, or fracture toughness, versus normalized crack length for two double-cleavage, drilled-compression specimens taken from the same billet. The toughness increase as the crack traverses the fiber is a measure of the incremental toughening from a single bridging fiber. The figure also illustrates the degree of reproducibility between specimens.

Fig. 3. Applied stress intensity factor versus normalized crack length for double-cleavage, drilled-compression specimens which contain a one-, two-, or three-fiber array at each end of the specimen. The reversal in magnitude of toughening increment for the two- and three-fiber specimens is consistent with the interfacial properties measured for these two specimens. See Table 1.

Initially, the applied stress intensity factor increased as the crack passed the fiber. At a distance of about 8-10 fiber radii past the fiber the applied stress intensity factor decreases indicating that the fiber is being steadily pulled from the matrix.

Representative data for DCDC specimens with monofilament arrays of one, two and three fibers are plotted in Fig. 3. Similar trends to the data in Fig. 2 were observed. The major exception is the lack of data points for crack lengths between approximately $12 \cdot (c/r)$ and $18 \cdot (c/r)$. In the figure the bounding data points have been connected by a straight line (linear decrease), which is probably not an exact representation of the toughening increment in this region. Due to the rapid acceleration of the crack, measurement of the stress and crack length in this region of these specimen was difficult. Most likely, the applied stress intensity factor dropped rapidly as the fiber(s) debonded or were pulled from the matrix.

The specimen which showed the largest increase in toughness was the specimen with two-fiber array. This observation was not expected because increasing the number of fibers in a given specimen cross-section is equivalent to increasing the fiber volume fraction and the toughening increment should increase with a larger volume fraction. Examining the fracture surfaces for the two and three fiber specimens, one sees a smooth planar fracture, indicative of mode I cleavage. There was some evidence of slight devitrification at the diffusion-bonded layer between the glass plates, but close observations of the interfacial region next to the fiber indicated such devitrification did not greatly influence the fiber-matrix interface.

Representative scanning electron micrographs of the fiber-matrix interface region are shown in Figs. 4a & 4b for DCDC specimens which contained two and three fiber arrays, respectively. The interface appears well bonded except for a small tapered void along the glass plate interface. The void for the two fiber specimen appears to be smaller than that for the three fiber specimen. This may indicate that the fibers in this specimen were more securely bonded than in the three fiber specimen, or that the greater fiber-matrix contact area resulted in a higher frictional pull-out resistance. The specimens were processed for different times at the maximum temperature to suppress devitrification along the interface, so that different interfacial properties are entirely possible.

(a)

(b)

Fig. 4. Scanning electron micrographs of representative monofilaments from double-cleavage, drilled-compression specimens which contain a (a) two- and (b) three-fiber array at each end of the specimen.

Such a speculation was supported by the single fiber pull-out tests. Measured values of the frictional shear resistance (debond strength) for the one fiber specimens ranged from 3.3 to 4.1 MPa (3.7 to 5.3 MPa), those for the two fiber specimen ranged from 3.7 to 4.9 MPa (5.3 to 6.4 MPa), and those for the three fiber specimens ranged from 3.2 to 3.7 MPa (5.4 to 8.2 MPa). Average data are shown in Table 1. Thus, the interfacial properties, specifically frictional shear resistance, of fibers in the one and three fiber specimens appear were similar, while those for the two fiber specimens were significantly greater. This increased frictional resistance resulted in an enhanced toughening increment. The final column of Table 1 confirms this. The percentage change in the toughening increment normalized by the concentration of fibers indicates a 22% increase for the two fiber specimen over that of an unreinforced matrix, while the one and three fiber specimens exhibit only an 11% enhancement.

Conclusions. The fiber-reinforced DCDC (double-cleavage, drilled-compression) specimen is a simple and versatile testing configuration for obtaining useful information about the interaction of cracks with reinforcing fibers in ceramic matrix composites. The single fiber pull-out test is a complementary technique for independently measuring the fiber-matrix interfacial properties. The combined testing procedure provides a systematic means for investigating relationships between processing, fiber-matrix interfacial properties and enhancements in material toughness.

Table 1. Processing conditions, average interfacial properties, and normalized toughening increment for one, two, and three fiber specimens.

Number of Fibers	Time at 705°C (min)	Debond Strength ^a (MPa)	Frictional Shear ^a Resistance (MPa)	$\delta(K_I)/K_{IC}$ per fiber
1 Fiber	135	4.2 ± 0.7	3.7 ± 0.3	11%
2 Fiber	120	6.0 ± 0.5	4.5 ± 0.6	22%
3 Fiber	90	6.6 ± 1.4	3.4 ± 0.3	11%

^a Average and standard deviation of four tests on 1 and 2 fiber specimens and of three tests on the 3-fiber specimens.

Real Ceramic Composite Systems

Creep Rupture Behavior of a SiC Whisker-Reinforced Alumina Composite

Summary. A ceramic composite material that has received much attention because of its increased toughness⁵ and creep resistance⁶ compared with alumina is aluminum oxide reinforced with silicon carbide whiskers. In this study, the creep and creep rupture behavior of a 25 wt% SiC whisker-reinforced alumina ceramic with 4.9% porosity were measured at temperatures between 1100°C and 1300°C and at applied stresses between 55 and 306 MPa, although the applied stresses at each temperature varied over a much narrower range. Creep strains were determined from loading-point displacement measurements in four-point flexure.

In the current reporting period, several long term tests were completed. Creep and creep rupture data were measured over a wide range of creep strains (0.05% to 2.0%) and failure times (0.3 to 1600 h). Failure times occur in two apparently different creep regimes: one characterized by a creep-hardening type behavior (higher applied stresses) and another in which this creep-hardening regime was followed by a long steady state regime (lower applied stresses). The transition in behavior from that at high stresses to that at low stresses is marked by a large change in failure time with only a small change in applied stress, for example, at 1300°C the failure time increases by a factor of 35 for a 16% decrease in stress. Transmission electron microscopy studies have shown that ruptured specimens from the low and high stress regimes do not display markedly different microstructural characteristics. The microstructure of the material has been modeled as an arrangement of elastic and viscous elements, and the experimental data was found to behave approximately as predicted for such a model.

Experimental Procedure and Results. The material studied was a 25 wt% (29 vol%) SiC whisker-reinforced alumina ceramic with 4.9% porosity. The material was provided as a billet through the courtesy of Dr. J. F. Rhodes of the Advanced Composite Materials Corporation. The techniques of creep specimen preparation and creep data collection have been described in the previous semiannual report⁷.

Three types of samples were prepared for transmission electron microscopy (TEM) studies: 1) material from the as-received billet; 2) material from the tensile region of specimens ruptured at 1300°C; and 3) material from the approximately 50 μm thick scale of the specimen tested at 1300°C and 72 MPa. The samples were cut as thin slices with a diamond saw. The samples from the ruptured specimen were cut parallel to the tensile surface. Disks 3 mm in diameter were ultrasonically cut from the slices and the disks were ground, dimpled, and ion-milled to perforation. TEM observations were made using conventional TEM, high resolution imaging, and selected area electron diffraction, operating at 120 and 300 kV.

The creep experiments, in progress at the time of the previous report, have either been completed or terminated. Some experiments lasted up to 1600 h (9.5 weeks). Table 2 gives a summary of the results. Two apparently different regimes of creep behavior were observed, as reported in the previous semiannual report⁷. Examples of both types of behavior are illustrated in the $\log(\text{strain})$ versus $\log(\text{time})$ data plotted in Fig. 5 for creep at 1300°C. For high stresses, the graph of $\log(\text{strain})$ versus $\log(\text{time})$ is approximately linear right up to the time of rupture. Such a creep response is typified by a creep-hardening behavior, which can be represented by:

$$\epsilon = Bt^a, \quad (2)$$

where a and B are constants. Both time-to-failure and strain-to-failure in this regime increased with decreasing applied stress. This type of behavior was observed by Porter⁸ at much higher temperatures (1500°C).

For low stresses, failure occurred during a long period of steady-state creep behavior following the creep-hardening regime. Steady-state strain rates in this regime were extremely small (as low as $10^{-11}/\text{s}$, which is the limit of the present measurement resolution). Several experiments at the smallest creep rates were terminated before failure; accordingly, there is a sparsity of data in the low stress regime. Although more data is needed, the strain at failure appears to decrease and the failure time to increase with decreasing applied stress.

Table 2. Creep rupture behavior of a 25 wt% SiC whisker-reinforced alumina composite with 4.9% porosity. Failure times and strains with a ">" symbol indicate the interrupted value for specimens which had not yet ruptured.

Temperature °C	Stress ^a (MPa)	Failure Time (hours)	Failure Strain ^a (percent)
1000	202	>359	>0.04
	301 ^b	>1229	>0.23
1000	249	>359	>0.04
	374 ^b	87	0.01
1100	231	139	0.18
	306	25.1	0.17
1116	200	865	0.53
	250	149	0.36
1124	126	>1588	>0.32
	149	>1588	>0.52
1145	175	262.4	0.62
	200	64.1	0.39
	224	35.6	0.39
	248	24.9	0.34
1200	123	>1170	>0.89
	124	>290	>0.45
	132	>52	>0.68
	147	60.8	1.18
	149	61	1.04
	174	19.9	0.83
	174	27.2	0.87
	198	12.3	0.70
	200	7.5	0.73
	249	0.32	0.15
1245	82	>756	>0.82
	98	161.7	1.14
	122	27.0	1.86
	147	7.5	1.17
1300	55	>1012	>0.31
	62	1001	1.07
	72	27.6	1.85
	98	5.1	1.96
	98	14	1.61
	124	16	0.87

^a Value calculated assuming a power-law-creep, stress exponent of unity.

^b Creep test continued at the higher applied stress from previous specimen.

Fig. 5. Logarithmic creep data at 1300°C [logarithm of creep strain versus logarithm of time] for flexural specimens of a 25 wt% SiC whisker-reinforced alumina composite with 4.9% porosity. Note the change in behavior between applied stresses of 62 and 72 MPa.

Optical microscopy of the as-received composite showed that the material consisted of regions 20 μm to 80 μm in diameter containing a relatively high density of whiskers separated by narrow bands about 5 μm wide with a lower whisker fraction. TEM examination of the as-received material revealed intragranular pores in the Al_2O_3 and cavities at a few of the junctions between whiskers and the Al_2O_3 grain boundaries, accounting for the 4.9% porosity. The whiskers are single crystals of β -SiC aligned along the $\langle 111 \rangle$ direction and faceted on $\{112\}$ planes, as originally reported by Nutt⁹, and the cavities were frequently found to be triangular prisms in shape, bounded by a $\{112\}$ SiC plane and two low-index Al_2O_3 planes, for example, a $\{0001\}$ plane. The cavitation between adjacent whiskers in the material was often more pronounced than next to isolated whiskers.

TEM observations were made on the microstructure of specimens tested at 62 MPa and 1300°C, and at 72 MPa and 1300°C with failure times/strains of 1001 h/1.07% and 28 h/1.8%, respectively. These specimens come from low and high stress regimes, respectively, and their failure times differ by a factor of 35, although the applied stresses differ by only 16%. Despite the large difference in time-to-failure between these two specimens, there was little difference between the observed microstructures. Figs. 6a and 6b are taken from the tensile regions of the specimens and both show considerably increased cavitation at the whisker/grain boundary triple junctions compared with the as-received material. The cavities were frequently lined with a thin layer of glass as seen clearly in Fig. 6a taken from the lower stress specimen; the glass is of the order of 50 nm thick and is adhering to both phases. The Al_2O_3 triple junctions displayed a much lower level of cavitation and glass decoration. Cavitation was the principal evidence of deformation observed in these specimens. Little dislocation activity was observed in the specimens beyond small angle grain boundaries in a few of the larger Al_2O_3 grains. The specimens were not removed from the furnace immediately after failure; in some cases the specimens were held at test temperature for several hours after failure, so it is possible that any dislocations generated during creep were annealed out of the Al_2O_3 grains before the dislocation structure was frozen in.

Since the specimens were tested in air, reaction layers (or scales) formed at their surfaces; previously polished surfaces had their finishes

(a) **(b)**

Fig. 6. Transmission electron micrographs of creep specimens tested to failure at 1300°C and applied stresses of (a) 62 MPa and (b) 72 MPa. The time-to-failure was 1,001 h at 62 MPa, but only 28 h at 72 MPa. Both microstructures show a high degree of cavitation at whisker/grain-boundary triple junctions.

dulled. Numerous pits were formed on the surface, which were on the order of 20 to 40 μm in diameter. The pits obscured microindents which had been placed on the side of the creep specimen to monitor any shifts in the neutral strain axis during creep. The microstructure of the scale close to the scale/composite interface where the specimen was taken consists of grains of alumina dispersed in a siliceous glass containing some Al and Ca, with occasional colonies of thin tabular mullite grains, $3(\text{Al}_2\text{O}_3) \cdot 2(\text{SiO}_2)$.

Discussion. The high-stress creep data and the primary portion of the low-stress creep data are in general well described by Eqn. (2) as can be seen from the practically linear plots of Fig. 5. A linear least-squares fit of the data to the logarithm of Eqn. (2) showed that the time exponent, a , lies in the range 0.35 to 0.75 and appears to remain fairly constant over a range of applied stresses at a given temperature. In general B increases with increasing stress at a given temperature.

An increase in cavitation was observed by TEM to be the principal deformation mechanism, within the limitations on dislocation observation noted above. There was little difference in microstructure between the two specimens observed despite their considerable differences in deformation behavior with time. Both specimens were studied after failure, in contrast to the observations of Lipetzky et al.¹⁰ who interrupted their creep experiments to make TEM observations once steady state had been reached. They found a change from glass pocket formation at grain boundary-interface junctions in a specimen from the low stress regime (35 MPa at 1300°C) to cavitation in a specimen in the high stress regime (100 MPa at 1300°C). Cavitation was observed in the present study in both stress regimes and also in the as-received material. Comparison of the two sets of microstructural observations is difficult because our specimens had failed whereas those of Lipetzky et al. had not, the starting materials had different porosities and the applied stresses differed considerably between the two studies. More systematic studies (preferably in tension) of cavitation as a function of strain are needed to determine the reasons for the apparent change in creep behavior between the low and high stress regimes. In addition, since the cavities observed were large enough to be visible in a scanning electron microscope, SEM studies of polished sections

taken from creep specimens would provide quantitative information (unobtainable in TEM) on the distribution of cavities in the material.

Porter⁸ has suggested that these composite materials, in their response to an applied stress, can be modeled as an elastic element (the network of SiC whiskers) in parallel with a viscous element (the alumina matrix); this Kelvin-Voigt compound model is in series with another viscous element representing the non-recoverable deformation of the composite which is caused by the incomplete nature of the whisker network and by broken whiskers. The strain-time response, $\epsilon(t)$, of such a model under load is:

$$\epsilon = k_1 \cdot [1 - \exp(-t/\tau)] + k_2 t, \quad (3)$$

where k_1 , k_2 and τ are constants related to the applied stress and the elastic and viscous constants of the model. This equation has been fitted to the data with partial success, although Eqn. (2) fits the primary creep data better.

Other models can be proposed. For instance the elastic element in the above model could be replaced with a perfectly plastic element which is rigid below a critical stress and flows at that stress; this element would attempt to represent the behavior of a SiC/Al₂O₃ interface with a glass coating. Alternatively, another elastic element could be inserted into the Kelvin-Voigt element in series with the dashpot to represent the elastic response of the alumina. Whatever mechanistic model is used to analyze the data should successfully match the complete creep behavior, including the primary creep, which is so well described rheologically by Eqn. (2). The fact that the initial regions of the plots in Fig. 5 are linear with slopes between 0.35 and 0.75 as discussed above suggests a modification to Eqn. (3) in which the argument of the exponent is raised to some power, a , as determined by fitting Eqn. (2) to the data.

One possibility is that the flexural test itself modifies the creep response. Collaborative research has been initiated with S. M. Wiederhorn of NIST to obtain tensile creep data on this material and with T.-J. Chuang of NIST to analyze the flexural data based upon tensile and compressive rheological models, such as Eqn. (3).

Conclusions. The creep data presented here for SiC whisker reinforced Al_2O_3 show two apparently different regimes of response to a range of applied stresses at a given temperature. Transmission electron microscopy of ruptured specimens in the two regimes indicates no major microstructural differences between them. The creep data have been fitted to a rheological equation that is based on a reasonable viscoelastic model of the composite material with partial success.

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ORNL-1(A) - FABRICATION OF CERAMIC FIBER-CERAMIC MATRIX COMPOSITES
BY CHEMICAL VAPOR INFILTRATION

D. P. Stinton, R. A. Lowden, and T. M. Besmann

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

The purpose of this task is to develop a ceramic composite having higher than normal strength and toughness yet retaining the normal ceramic attributes of refractoriness and high resistance to abrasion and corrosion. Ceramic fiber-ceramic matrix composites are being fabricated by infiltrating fibrous structures with vapors that deposit on and between the fibers to form the matrix of the composites.

Background

Fiber composites are in the limelight as a result of exceptionally high toughness values recently achieved for glass ceramics reinforced with silicon carbide fibers. Because use of ceramics is frequently restricted by inadequate toughness, any progress toward toughening ceramics will greatly expand their potential market. However, a generic problem that must be overcome is that normal ceramic fabrication processes tend to damage fibers mechanically and chemically when the fibers are consolidated within a ceramic matrix. The purpose of this task is to form the matrix by a comparatively low-stress, low-temperature chemical vapor deposition (CVD) infiltration process that will avoid the pitfalls of conventional ceramic processing.

As reported previously, others have used CVD infiltration for fabricating ceramic composites. The vapor consolidation technique has been used to prepare fiber composites with matrices of carbon and/or such ceramics as SiC, Si₃N₄, B₄C, BN, and TiB₂.

App each

Our goal is to demonstrate a rapid process for fabricating, via chemical vapor infiltration (CVI), a ceramic fiber-ceramic matrix composite consisting of materials of high interest to the fossil energy community. An initial assessment identified SiC fibers and matrices of Si₃N₄ and SiC as being promising. An infiltration process utilizing a thermal gradient combined with forced flow of the reactants is being pursued.

DISCUSSION OF CURRENT ACTIVITIES

Ceramic composites consisting of continuous, high-strength Nicalon (SiC) fibers incorporated into brittle SiC matrices exhibit increased fracture toughness and are of tremendous interest to the ceramic community. The increased fracture toughness that prevents catastrophic failure of the composite is a result of dissipation of crack propagation energy as fibers pull out of the matrix and crack deflection at crack-fiber interfaces. Fiber-reinforced ceramic composites exhibiting these properties are being fabricated by forced chemical vapor infiltration at ORNL. In recent months, a goal of this program was to identify alternate reinforcements that resulted in materials with promising mechanical properties. Therefore, composites were fabricated from various types of continuous fibers other than Nicalon. The alternatives investigated included Nextel aluminosilicate and Tyranno SiC fibers. Also of interest are whicker and platelet reinforcements. Composites were fabricated from preforms supplied by American Matrix Inc. and the Naval Surface Warfare Center (NSWC). American Matrix preforms were fabricated from SiC platelets and from SiC whiskers. The NSWC supplied several preforms made from mullite whiskers. Composites fabricated from each of these materials will be described.

In order for the forced CVI process to operate effectively, a proper temperature gradient with appropriate cool face temperature must be established within the preform. Since the thermal conductivity of preforms fabricated from different reinforcements varied considerably, a thermocouple was placed in contact with the cool side of the composite to

determine the thermal gradient. Measurements were taken for composites fabricated of Nicalon cloth, Nextel cloth, SiC platelets, SiC whiskers, and mullite whiskers. For these measurements, the hot face was held at 1455 K and the cool face temperature was measured (Table 1). Clearly, the composition of the materials, the packing, and type of material affect the bottom temperature.

Table 1. Measurement of cool face temperatures for various preforms

(hot face temperature = 1455 K)

Preform	Fiber (vol %)	Cool surface temperature (K)
Nicalon cloth	40	995
SiC whiskers	12	1025
SiC platelets	35	1115
Nextel cloth	40	1015
Mullite whiskers	26	925

Several composites were fabricated using SiC platelet preforms. The high thermal conductivity of these preforms resulted in unusually high cool face temperatures. Therefore, the hot face temperature for infiltration was reduced by 150 K in an attempt to produce the appropriate temperature gradient. The preforms were not completely infiltrated at the cool surface for these conditions, but the infiltration of the top and middle was sufficient to determine approximate flexural strengths (Table 2). Optimization of the infiltration conditions and temperature gradient could be performed to produce uniform densities throughout the composite. Fracture toughness of flexure bars cut from the top surface were measured by single-edge notched beam to be only $2.2 \text{ MPa} \cdot \text{m}^{1/2}$.

Several preforms were fabricated from SiC whiskers supplied by American Matrix Inc. Despite the low fiber content (10 vol %), the thermal conductivity of the preform was higher than that for Nicalon cloth preforms (see Table 1). Therefore, standard infiltration conditions were used to fabricate several composites. Since the infiltration conditions were not optimized, the densities of the composites were somewhat low and

Table 2. Characterization of composites reinforced with SiC platelets

Sample	Fiber content (vol %)	Sample location	Composite density (percent theoretical)	Flexural strength (MPa)
PL-1	35	Top	77.8 ± 0.5	71.8 ± 13.2
230	35	Top	87.0 ± 0.7	122.1 ± 9.8
		Middle	81.3 ± 2.5	102.8 ± 17.4
223	35	Top	89.2 ± 1.5	137.7 ± 4.0
		Middle	85.4 ± 0.6	106.2 ± 0.9
		Bottom	73.8 ± 3.8	98.5 ± 1.2

the density in the middle of sample 222 was higher than the density of either the top or bottom of the composite. The mechanical properties of these composites are shown in Table 3. Fracture toughness of flexure bars cut from sample 222 were measured to be about $5.0 \text{ MPa}\cdot\text{m}^{1/2}$.

Several mullite whisker preforms fabricated by NSWC were supplied to ORNL, and one of the preforms was infiltrated. The mullite whiskers were grown from a powder compact and nucleated to form floret-shaped crystals. Because the thermal conductivity of these preforms was much lower than the SiC whisker preforms (see Table 1), a higher temperature was used for the initial infiltration conditions. Densification of the initial preform was

Table 3. Characterization of composites reinforced with SiC and mullite whiskers

Sample	Fiber content (vol %)	Sample location	Composite density (percent theoretical)	Flexural strength (MPa)
W-3	12 (SiC)	Top	81.4 ± 3.7	254.5 ± 51.2
		Middle	72.9 ± 2.2	230.7 ± 39.7
222	10 (SiC)	Top	81.8 ± 0.6	126.3 ± 4.3
		Middle	90.3 ± 0.4	155.6 ± 3.9
		Bottom	67.0 ± 4.0	128.4 ± 44.7
235	26 (Mullite)	Top	84.0 ± 4.0	72.5 ± 10.8
		Middle	85.8 ± 2.5	78.1 ± 4.8
		Bottom	84.7 ± 1.3	93.6 ± 6.8

reasonably thorough and resulted in the mechanical properties shown in Table 3. The whisker size is larger than desired, but the fracture surface clearly shows that the whiskers interrupt the propagation of cracks. It also appeared that the whiskers were not distributed uniformly throughout the preform. The nonuniform distribution of fibers resulted in a lower fracture toughness ($\sim 3 \text{ MPa}\cdot\text{m}^{1/2}$).

Fiber-reinforced composites from Nicalon cloth have good room-temperature mechanical properties; however, the strength of the fibers degrades significantly during processing. Therefore, fabrication of composites from alternate fiber types that retain their strength at elevated temperatures is of significant interest. During this investigation, a limited number of composites were fabricated from Al_2O_3 , Nextel, and Tyranno fibers. Aluminum oxide fibers are of interest because of their high modulus and potential improvement in high temperature creep. Unfortunately, the high modulus makes the fibers very fragile and difficult to handle or weave. A composite fabricated from Al_2O_3 cloth was infiltrated and had the mechanical properties shown in Table 4.

Nextel fibers are of interest in the composite community because of their availability and ease of handling and weaving. Composites fabricated from Nextel fibers were not as thoroughly infiltrated as the Al_2O_3 fibers; however, the mechanical properties were somewhat more encouraging. The thermal conductivity of the Nextel preforms was surprisingly similar to that of Nicalon preforms (Table 1). The load displacement curves for both Nextel and Al_2O_3 cloth are shown in Fig. 1. Both composites exhibit toughening by fiber pullout, but the fracture is more brittle than for composites reinforced with Nicalon fibers.

Tyranno fibers were investigated because of the potential improvement in high-temperature stability over that of Nicalon which has been reported. A second advantage of the Tyranno fibers is their smaller diameter (8 vs 15 μm) which results in improved behavior during handling, weaving, and braiding. The mechanical properties of composites reinforced with Tyranno fibers were very encouraging. Despite the slightly low density, strengths greater than 350 MPa (50 ksi) were obtained for the top, middle, and bottom of the composite. A load displacement curve for a Tyranno reinforced composite exhibits toughening by fiber pullout; however, the fracture is more brittle than for Nicalon composites (Fig. 1).

Table 4. Characterization of composites reinforced with continuous fibers

Sample	Fiber content (vol %)	Sample location	Composite density (percent theoretical)	Flexural strength (MPa)
208	21 (Al ₂ O ₃)	Top	85.9 ± 0.9	127.7 ± 21.7
		Middle	74.7 ± 4.4	147.5 ± 28.2
		Bottom	78.9 ± 3.0	164.8 ± 19.2
214	40 (Nextel)	Top	75.7 ± 0.7	184.9 ± 56.4
		Middle	73.7 ± 0.7	188.7 ± 8.2
		Bottom	66.7 ± 1.1	148.1 ± 21.4
215	34 (Nextel)	Top	75.6 ± 0.6	110.9 ± 10.8
242	43 (Tyranno)	Top	79.4 ± 1.8	395.4 ± 18.4
		Middle	75.6 ± 0.2	395.0 ± 7.5
		Bottom	72.5 ± 0.5	351.9 ± 11.0

Fig. 1. Load displacement curves for Nextel, alumina, and Tyranno cloth composites.

A major objective of this program in recent months has been the fabrication of composite samples for testing and evaluation by industry and other laboratories. Composite samples have been fabricated and cut and ground for the individuals and organizations listed in Table 5. Ten additional samples 7.5 cm in diameter have been produced and will be distributed to various organizations in the coming months.

Computerized equipment for the real-time control of process variables such as temperatures, reactant flows, and system pressures during infiltration was installed and interfaced with the control instrumentation. This equipment currently is being used to monitor the process variables mentioned earlier. During the next year, the model being developed at Georgia Tech Research Institute will be used to predict optimum infiltration conditions. Eventually, the computerized equipment will provide for controlled variation of the process variables throughout a run to optimize first the infiltration of the fine void volume within fiber bundles and second the infiltration of the larger void volume between fiber bundles.

Table 5. Composite samples for testing and evaluation

Individual	Company
1. Bill Ellingson	Argonne National Laboratory
2. John Walter	Idaho National Laboratory
3. Paul Grosskopf	Virginia Polytechnic Institute
4. Ed Fuller	National Institute of Standards and Technology
5. Judy Todd	University of Southern California
6. Chris Schilling	Pacific Northwest Laboratory
7. L. H. Schoenlein	Pacific Northwest Laboratory
8. John Brennen	United Technology Research Center
9. Sal Riccatello	NASA Ames Laboratory
10. Frank Kustas	Martin Marietta Aerospace, Denver
11. Steve Novak	Charles Evans and Assoc.
12. Jay Morrison	Rolls Royce Inc.
13. August Muhlratzer	MAN Technologie*

*Samples currently being fabricated.

ORNL-1(C) - CHARACTERIZATION OF FIBER-CVD MATRIX INTERFACIAL BONDS

R. A. Lowden, D. P. Stinton, and T. M. Besmann

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

The purpose of this task is to optimize the strength and toughness of fiber-reinforced ceramic composites by controlling the bonding and frictional stresses at the fiber-matrix interface. Methods must be developed to characterize fiber-matrix interactions and measure interfacial stresses in fiber-reinforced ceramic composite systems. Coating or pretreatment processes can then be utilized to tailor the fiber-matrix interfacial stresses within various composite systems and to optimize the strength and toughness of the composite.

Background

Production of low-cost ceramic fibers with improved strength has spurred the development of fiber-reinforced ceramic composites for high-temperature applications. The stresses at the fiber-matrix interface influence the mechanical properties of the composites. Very strong bonds result in brittle fracture because cracks propagate through both the matrix and the fiber. Extremely weak bonds between matrix and fiber fail to transfer the load from the matrix to the fiber, and the mechanical properties of the composite are thus limited by the properties of the matrix. Composites with both high strength and adequate fracture toughness can only be obtained by transferring the load to the fiber while exhibiting significant fiber pullout.

Pyrolytic carbon coating of Nicalon fibers by Amercom and Refractory Composites resulted in improvements in mechanical properties in SiC matrices. The strength of the interfacial bond between the SiC matrix and the Nicalon fiber was reduced, which resulted in increased fiber pullout and improved fracture toughness. The effect of controlling interfacial

bond strengths must be investigated and understood so that fiber pretreatments or coating processes can be developed which optimize the strength and fracture toughness of various composite systems.

Approach

The goal of this project is to demonstrate that the interfacial bond between Nicalon fibers and various ceramic matrices can be measured and controlled for optimization of mechanical properties such as strength and toughness. The technical approach to be followed during this project includes four tasks: (1) develop interface characterization techniques, (2) develop bond strength measurement techniques, (3) determine candidate overcoat compositions and develop overcoating of fibers, and (4) characterize composites and correlate fiber-matrix bonding with strength and strain tolerance.

Fiber-matrix bonding and interfacial frictional stresses in this and other systems clearly influence load transfer and fiber pullout in fiber-reinforced composite systems and, thus, control the fracture toughness of the material. Techniques will be developed to investigate the interfacial region and determine the effect of intermediate layers on the bond strength and frictional stresses and their effects on the resulting fracture toughness of the composite. Methods will be developed to measure the bond strength and interfacial frictional stress in fiber-reinforced composite systems, or at least to determine the relative stresses of one fiber-matrix system as compared to another.

Once fiber-matrix interfaces can be characterized and bond strengths can be measured, methods such as fiber pretreatment or application of interfacial layers will be developed to modify and control the fiber-matrix bonds. Processes will be developed to apply the selected overcoat materials to Nicalon fiber tows or to Nicalon cloth in quantities necessary for composite fabrication. Mechanical properties of optimized composites, including room-temperature strength, high-temperature strength, and fracture toughness, will be determined and correlated with the fiber-matrix bond strengths.

DISCUSSION OF CURRENT ACTIVITIES

Fiber-Matrix Bond Measurements

The fiber-matrix interfacial forces in a composite strongly influence the strength and fracture behavior of the material. A weakly bonded interface leads to a low matrix fracture stress and low ultimate strength. As the composite is stressed, load is not transferred from the matrix to the fibers; thus, the properties of the reinforcement are not utilized efficiently. As cracks are generated, they progress as in a porous ceramic material, and upon complete matrix failure the fibers are pulled from the matrix with little resistance. An increase in interfacial friction yields a higher matrix cracking stress by hindering crack propagation and by utilizing the properties of the fibers through effective load transfer prior to matrix failure. Higher ultimate strength is also achieved because more energy is expended to overcome the interfacial forces to pull the fibers out of the matrix. An extremely strong bond does not allow for crack deflection or debonding at the fiber-matrix interface; therefore, a crack propagating in the matrix simply passes through the fibers undisturbed, resulting in brittle fracture. A median position between high matrix failure stress and ultimate strength must be chosen to obtain the gradual composite failure through effective fiber pullout.

Several methods for quantifying the strength of interfacial bonds in fiber-reinforced composites have been investigated.¹⁻⁵ Such tests utilize relatively simple load and displacement relationships to determine bond strengths and interfacial frictional stresses. A common technique is the indentation method, which has been thoroughly examined. This technique involves using a microhardness indenter to apply a force to the end of a fiber embedded in a matrix. Interfacial shear stresses can be evaluated from the applied load and the displacement of the fiber. The interfacial shear stress is calculated from impression dimensions on the fiber end and the contact points along the edge of the fiber cavity.

Marshall's analysis¹ of the forces needed to displace a fiber in a thin specimen yields

$$F = 2\pi R\ell\gamma, \quad (1)$$

where γ is the frictional stress, t is the thickness of the sample parallel to the direction of the fibers, and R is the cylindrical fiber radius. This relationship holds for thin specimens in which the thickness of the sample is less than the sliding distance of the fiber. The fiber will thus simply be pushed out of the opposite surface when a load is applied. The analysis becomes much more complex if the thickness of the specimen is larger than the sliding distance; however, approximate results can be obtained from the relationship for thicker specimens if the thickness of the specimen is much greater than the sliding distance. The frictional stress can then be calculated from the displacement of the fiber, u , due to the load imposed by the diamond indenter. The frictional stress is

$$\gamma = F^2 / 4\pi^2 u R^3 E_f , \quad (2)$$

where E_f is the Young's modulus of the fiber and u is the fiber displacement. The value of u can be determined from the indent impression dimensions on the fiber, a , and on the edges of the fiber cavity, b , and the indenter angle, s ,

$$u = (b - a) \cot \phi/2 . \quad (3)$$

The force supported by the fiber, F , can be obtained from hardness impressions on the fiber,

$$F = 2a^2 H , \quad (4)$$

where H is the hardness of the fiber.

The expressions for calculating interfacial frictional stresses are applicable to Nicalon fibers which have circular cross sections; however, they cannot be directly applied to irregularly shaped fibers. Nextel fibers possess an oval cross section, and thus the equations must be modified to account for the changes in surface and cross-sectional areas. The cross-sectional area of the Nextel fiber can be approximated as simply a combination of a rectangle with half circles at opposing ends. The cross-sectional area of the filament thus becomes

$$A_f = \pi \omega^2 / 4 + \omega(L - \omega) , \quad (5)$$

where w is the width and L is the length of the fiber cross section. The surface area of the fiber is given by

$$A_s = [\pi w + 2(L - w)]l, \quad (6)$$

with l being the fiber length. Substituting these equations into Eq. (2), interfacial frictional stress can be calculated from the indent impression dimensions using

$$\gamma = \frac{F^2}{2E_f u [\pi w^2/4 + w(L - w)] [\pi w + 2(L - w)]}, \quad (7)$$

with the variables being the same as in Eq. (2). The force (F) and fiber displacement (u) are determined utilizing Eqs. (3) and (4) with the exception that the indenter will only contact the edges of the cavity across the width of the fiber.

Effect of Temperature and Environment on Nicalon Fibers

Nicalon fibers exhibit strength loss upon heating and during the pre-coating and infiltration processes. The degradation of properties is caused by structural and compositional changes that occur during processing. The effects of coatings and heat treatments on the strength and stability of the fibers are being investigated. The tensile strengths of fiber tows coated with intermediate layers and heat treated to simulate processing conditions are being measured and the microstructure and composition of the fibers are being examined using X-ray diffraction, transmission electron microscopy, and other electron microscopic techniques. Table 1 is a list of measured mechanical properties of Nicalon fibers subjected to various treatments. Although the fibers retain much of their strength during the deposition of various intermediate layers, fiber strength decreases upon heating to infiltration temperatures.

A carbon layer deposited on fibrous preforms prior to densification improved the mechanical properties of Nicalon/SiC composites fabricated using forced-flow, thermal-gradient chemical vapor infiltration (FCVI) techniques (Table 2). Precoating fibers prior to matrix deposition not only reduced interfacial stresses, but may have also provided protection

Table 1. Strength and modulus for treated Nicalon fibers

Treatment	Strength (MPa)	Modulus (GPa)
From references 6 and 7:		
As received	1766	106
Sizing removed ^a	2110	118
800°C Ar	1310	
1000°C Ar	1283	
1200°C Ar	1234	108
1300°C Ar	1262	110
1400°C Ar	848	104
1200°C air	660	110
1300°C air	1262	114
1400°C air	1379	102
1000°C vac	690	
1200°C vac	345	94
1300°C vac	200	48

Tested at ORNL:

Uncoated continuous	2315 ± 160
Uncoated from cloth	1730 ± 126
Carbon coated	2175 ± 191
Silicon coated/HT ^b 1475 K	0 ^c
Boron coated	861 ± 70
Boron coated/HT 1475 K	163 ± 40
BN coated ^d	1886 ± 464
BN coated ^e	1718 ± 304
BN coated ^d /HT 1475 K	539 ± 68
1275 K 10% HCl/H ₂ 1 h	1847 ± 99
1375 K 10% HCl/H ₂ 1 h	1223 ± 89
1475 K 10% HCl/H ₂ 1 h	861 ± 70
1475 K 10% HCl/H ₂ 25 h	71 ± 15

^aSizing removed by passing through open flame.^bHT = heat treated to specified temperature.^cFailed during heat treatment.^dPurchased from Synterials, Herndon, VA.^eFrom diborane/ammonia mixture at 875 K and 3 KPa.

Table 2. Intermediate coatings and their effect on interfacial stress and mechanical behavior

Precoating	Thickness ^a (μm)	Flexure strength (MPa)	Frictional stress (MPa)	Observed behavior
<i>Nicalon</i>				
Uncoated		82 + 10	49 + 15	Brittle
Silicon	0.17	88 + 8	118 + 61	Brittle
Boron	0.50	107 + 15	6.3 + 1.7	Brittle
Carbon	0.03	108 + 13	25 + 14	Brittle
Carbon	0.07	262 + 11	11 + 5	Low pullout
Carbon	0.12	390 + 13	0.6 + 0.4	High pullout
Boron nitride	0.15	256 + 93	--	Pullout
<i>Nextel 440</i>				
Uncoated		61 + 35	76 + 38	Brittle
Carbon	0.40	172 + 30	0.8 + 0.3	High pullout

^aCalculated from weight gain.

from chemical attack during processing. The fiber-matrix interfacial stresses were modified by varying the thickness of the carbon layer. The influence of the thicknesses on resultant interfacial frictional stresses, which ultimately affect matrix cracking stress and postfracture behavior, is shown in Fig. 1.

Preforms containing Nextel 440 alumino-borosilicate fibers, with and without a carbon intermediate coating, have been infiltrated with SiC. The interfacial frictional forces have been measured using the indentation

Fig. 1. The effect of varying thickness of pyrocarbon on the flexure behavior of SiC composites.

technique described above. The composites have been tested in four-point bending to determine flexure strength and to observe fracture behavior. The results are listed in Table 2 along with results for Nicalon/SiC composite with various interlayers.

The composite containing uncoated Nextel fibers possessed low strength and showed no evidence of fiber pullout. This behavior appears to be due to a combination of strong bonding and fiber property degradation. Nextel is an alumino-borosilicate fiber which is prone to chemical attack by the chloride byproducts that are generated during infiltration.

The chemical reactions that occur during densification degrade fiber properties and enhance bonding at the fiber-matrix interface. The sample fabricated from carbon-coated Nextel fibers showed improved properties and reduced interfacial bonding. The carbon likely acted to weaken the bonding and friction at the fiber-matrix boundary and protected the fibers from damage during processing.

Samples of Nicalon plain-weave fabric have been coated with thin layers of boron nitride by Comhurex's CVD Division. Preforms have been fabricated from cloth with a 0.15- μ m coating of BN and the samples have been infiltrated with SiC. The composites have been tested in four-point bending to determine strength and observe fracture behavior. The results are listed in Table 2. The BN-coated specimens demonstrated moderate flexure strengths as compared to composites fabricated from carbon-coated fibers, and the samples exhibited fiber pullout and extended strain to failure. Microindentation testing of this system has not yet been performed.

The results of the aforementioned indentation techniques are only semiquantitative. The techniques cannot distinguish between debonding and frictional stresses. These are two distinct phenomena that influence the mechanical behavior of a composite, and thus the influence of each must be determined. It has been shown that the independent events of debonding and slip can be examined utilizing instrumented indentation techniques. The Nanoindenter has been used to investigate these phenomena in glass-ceramic matrix composites;³ however, the instrument is limited by its low load capabilities. Work has been initiated to improve the loading system of the Nanoindenter and increase the usable loading range.

Instrumented microhardness indentors have been constructed to simultaneously record load and displacement during indentation.⁸ These instruments employ standard indentors equipped with load and displacement devices and thus are capable of loads up to 20 N. A standard hardness indenter is being equipped with a load cell, and capacitance displacement devices and will be used to determine the individual stress components of bonding and friction at the interface in fiber-reinforced composites.

Precoating Bulk Ceramic Fabric

In the past, intermediate coatings have been deposited on completed cloth preforms. A spacer is placed between the water-cooled gas injector and the preform to produce an isothermal hot zone and the coatings are then deposited at low pressure using low reactant concentrations to ensure uniformity throughout the preform. The procedure has yielded relatively uniform coatings in the small 45×13 mm disk-shaped samples but has not been entirely successful when applied to thicker 75-mm-diam samples. The thickness of the intermediate coating varies throughout the preform and this variation could be larger in more complex shapes. The question of uniformity and the potential difficulties that may arise in the deposition of layers from more complex gas systems have led to the investigation of alternate processes for depositing the intermediate coatings. Application of the coatings to the individual filaments within the yarns prior to weaving would be ideal; however, this process may be impractical as the weaving processes would likely damage the coatings. Therefore, a process to coat large sections of fabric has been investigated.

A furnace system large enough to coat pieces of the fabric before preform fabrication has been assembled. A furnace with a 1.0×0.2 m hot zone was equipped with a specialized gas injection system that is capable of distributing the reactant gases evenly throughout the coating chamber. Uniform coatings have been applied to the cloth before it is cut and stacked in the holder. Carbon coatings have been applied to 0.25×0.75 m pieces of Nicalon plain-weave cloth. The carbon layers were deposited on woven fabric from a propylene/argon gas mixture at 1275 K and a pressure of 5 kPa. The thickness of the coatings were varied by changing the concentration of the propylene in the gas mixture.

Fabric with a thin carbon coating (<0.1 mm) retained flexibility while a thicker coating (>0.2 mm) stiffened the cloth. Preforms were fabricated from the coated fabric to investigate damage that may occur during preform assembly. The cloth layers were then removed from the graphite holder after stacking and compression and optical and scanning electron microscopic analysis of the coated cloth showed no damage to the coatings. Henceforth, composite samples will be fabricated from pre-coated cloth, and the properties of the samples will be compared to those

of composites previously fabricated from preforms coated in the holder utilizing the original technique.

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ORNL-1(D) - MICROWAVE SINTERING OF SUPERCONDUCTING CERAMICS

H-E Kim and W. B. Snyder

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

The purpose of this task is to sinter the high critical-temperature (T_C) superconductor ($YBa_2Cu_3O_{7-x}$) by microwave heating. By utilizing microwave heating, which has been found to be effective in lowering the sintering temperature of alumina and zirconia, it may be possible to lower the sintering temperature of the high- T_C superconductor. By lowering the sintering temperature of the superconductor, the detrimental effects of phase transformation from tetragonal to orthorhombic phase during cooling after sintering can be minimized and, consequently, the critical current density, J_C , of the superconductors can be increased. Sintering experiments of the high- T_C superconductor have been performed in a 2.45-GHz microwave furnace at various temperatures and times. Results showed that the superconductor can be sintered at lower temperatures in the microwave furnace than in the conventional resistance furnace. The J_C of the superconductor sintered in the microwave furnace was higher than that sintered in the conventional resistance furnace.

DISCUSSION OF CURRENT ACTIVITIES

Superconductor powder was prepared by conventional solid state reactions. A stoichiometric mixture of Y_2O_3 , CuO , and $BaCO_3$ was milled in isopropyl alcohol. After milling, all the isopropyl alcohol was removed from the powder in a vacuum evaporator. The dried powder was pelletized and calcined in a conventional resistance furnace in air. After firing, the powder was ground and milled again. This process was repeated three times to obtain clean superconductor phase. Figures 1(a) and (b) show the morphology and size distribution of the powder, respectively, used for this experiment.

T000807

(a)

88-15089

(b)

Fig. 1. Superconductor powder used for the microwave sintering. (a) Microstructure. (b) Particle size distribution.

The following sintering experiments were done. First, direct heating of the superconductor was tried. To sinter the superconductor directly, it should be insulated with some materials which are inert with respect to the superconductor. Alumina; zirconia; boron nitride; magnesia; a mixture of Y_2O_3 , $BaCO_3$, (BaO_2) , and CuO ; and superconductor powder were tried as insulating materials. None of these materials were suitable as an insulating material because of the reaction with the superconductor or arcing with the thermocouple. This method will not be used until some material stable with respect to the superconductor is found.

Second, a combination of direct and indirect heating of the superconductor using a susceptor was tried. In this technique, superconductor pellets were inserted in alumina crucible and were surrounded by alumina fiber and a conducting ceramic. Superconductors could be sintered in this way. The relative densities of the superconductors sintered with this technique are shown in Fig. 2, along with those sintered by conventional resistance heating. These results show clearly that the superconductor can be sintered at a lower temperature in the microwave furnace than in the conventional resistance furnace. It was also observed that the superconductors sintered in the microwave furnace have different microstructures from those sintered in the conventional resistance furnace. The microstructures of the superconductors sintered in the microwave furnace and conventional furnace are shown in Fig. 3. These micrographs show that strong anisotropy was developed in the grains of the superconductors sintered in the microwave furnace. This anisotropy is potentially beneficial to the electrical and mechanical properties of the superconductor. The J_c of the superconductors are compared in Fig. 4, which shows that J_c of the superconductors sintered in the microwave furnace were higher than those for superconductors sintered in the conventional resistance furnace. The relatively low J_c observed are believed to be the results of the high sintering temperatures due to the large particle size, and short sintering and annealing time (2 h each). Even though J_c of both superconductors were not satisfactorily high enough, the tendency of higher J_c in the superconductor sintered in the microwave furnace is apparent. By optimizing the sintering conditions, higher J_c will be obtained.

Fig. 2. Relative density of the sintered superconductors.

T000812

T000819

Fig. 3. Surface morphology of the sintered superconductors. (a) Sintered in the microwave furnace. (b) Sintered in the conventional resistance heating furnace.

Fig. 4. Critical current density of the superconductors.

PNL-1 - IMPROVED CERAMIC COMPOSITES THROUGH CONTROLLED
FIBER-MATRIX INTERACTION

R.H. Jones, L.H. Schoenlein, C.H. Henager, Jr.,
C.H. Schilling, N. T. Saenz and J.L. Bates

Pacific Northwest Laboratory
P.O. Box 999
Richland, Washington 99352

INTRODUCTION

Interfaces between whiskers or fibers and the matrix of ceramic composites play a crucial role in the performance of these materials. However, very little is known about the chemistry and structure of these interfaces and their relationship to composite properties. The purpose of this research is to gain an understanding of the relationship between the interfacial chemistry and structure and the composite properties, and to apply this understanding to control their properties. The goal is to optimize the interfacial and composite properties for fossil energy relevant temperatures and corrosive environments and ultimately to improve the performance of fossil energy systems.

This research is being conducted in the following three tasks: 1) interface characterization; 2) property evaluation; and 3) interface control. These tasks are interrelated so that Tasks 1 and 2 provide information that can be used to optimize the properties of ceramic composite materials. Information about the structure and chemistry of interfaces in ceramic composites is being obtained with transmission/scanning transmission electron microscopy (TEM/STEM) and Auger electron spectroscopy (AES). This information will be correlated with composite processing parameters and related to the fracture properties measured in Task 2. Also, micromechanical models of ceramic composite strengthening are being

evaluated for guidance in the selection of optimum interfacial properties.

DISCUSSION OF CURRENT ACTIVITIES

Interfacial Microstructure of SiC - Reinforced SiC

The brittle nature of ceramic materials is responsible for their susceptibility to catastrophic failure. The reinforcement of ceramic bodies with high-strength, high modulus ceramic whiskers (or fibers) is currently under intensive investigation as a means to strengthen these materials. Current theories suggest that microcracking (1), crack deflection (2), and crack bridging (3, 4) are the predominant toughening mechanisms, although the relative contributions of each mechanism to toughening have not been clearly delineated. However, there is general agreement that the interfaces between the whiskers and the matrix are of prime importance in enhancing toughness. Weakly-bonded interfaces significantly enhance the toughness of composites by facilitating crack bridging and whisker pullout during crack propagation, while strongly bonded interfaces facilitate whisker fracture which yields little or no increase in fracture resistance.

It is often necessary to coat the whiskers with an inert substance to prevent interfacial reactions between the whiskers and the matrix during fabrication of the composites as these reactions are likely to cause strong interfacial bonding. The type of coating materials and its thickness may be varied to yield interfacial phases which, in addition to preventing interfacial reactions, optimize the toughness of the composite. It is anticipated that composites will be used at elevated temperatures in severe environments, so interfacial phases which also have good oxidation and corrosion resistance will be required to minimize slow crack growth.

Experimental Procedure

The interfacial chemistry and phases of SiC-reinforced SiC composites have been evaluated by ultra-thin section transmission optical microscopy, (TOM), transmission electron microscopy (TEM), with associated x-ray energy dispersive spectroscopy, (EDS), microanalysis, and Auger electron spectroscopy, (AES). NicalonTM fiber reinforced SiC prepared by chemical vapor infiltration, (CVI), at Oak Ridge National Laboratory has been evaluated. Composite materials prepared with uncoated and Si coated fibers were examined by ultra-thin section, TOM and materials prepared with uncoated and BN coated fibers were examined by TEM.

Samples for TOM were initially prepared by vacuum-impregnation with a low viscosity thermosetting epoxy resin. The mounted samples were hand-lapped with a 30-micrometer metal bonded diamond wheel. The hand polished surface was then vibratory polished for 6 hours using a 1-micrometer diamond oil slurry on a stainless steel mesh polishing cloth, followed by 12 hours of vibratory polishing using aqueous slurry of 0.06 micrometer colloidal silica on a silk polishing cloth.

Upon completion of the first side, the samples were subsequently sliced with a diamond saw to produce a thin wafer having a surface parallel to the originally polished surface. This thin wafer was vacuum impregnated using the same resin as previously used and mounted on a 120 grit SiC belt, followed by hand-polishing with 60- and 30- micrometer metal-bond diamond wheels to reduce the sample thickness to approximately 20 micrometers. The surface was then vibratory polished using the procedures described above, until the desired thickness was achieved.

Specimens for TEM analysis were sectioned from the composites with a low speed diamond saw and mechanically polished to a thickness of $\approx 50\mu\text{m}$. Circular discs 3mm in diameter were core drilled from the polished sections, mounted on Mo washers, and ion

milled with 6 kV Ar ions at an angle of incidence of 15° until perforation was achieved. Carbon coating was not required on the whisker reinforced composite thin sections; the conductivity of the whiskers was adequate to prevent charging in the electron microscope. TEM analysis was performed with a Phillips EM400T electron microscope equipped with a Kevex Ultra-Thin x-ray detector and a Tracor-Northern multichannel analyzer.

Discussion

The structure of SiC fiber reinforced SiC prepared by the CVI process is illustrated in Figures 1-3. Examples are shown of reflected and TOM of material prepared with uncoated, Figure 1, and Si coated, Figures 2 and 3, NicalonTM fibers. Growth of the SiC during infiltration can be seen to occur by nucleation from the fibers and radial outward growth. A growth interface and porosity results at the intersection of the radially growing material. This growth interface could trap impurities ejected from the growing SiC or impurities in the infiltrating gas stream. These interfaces are potential fracture paths if their fracture strength is decreased by entrapped impurities or due to incomplete bonding or growth across the interface.

Other features apparent in these micrographs include the adherence of the Si coating, detached Si particles and SiC nucleation sites. The Si coating exhibits excellent adherence with only a few locations with bubbles or debonded material. Particles trapped within the SiC matrix are apparent in Figure 2. The chemical composition of these particles has not been determined; however, they appear to be Si particles that grew on the Si layer and dislodged during infiltration. Nucleation of the SiC from the fiber surface is apparent in Figures 1a and 3. The nucleation sites appear to be small features on the fiber surface as shown in Figure 3b. Also, the density of these nucleation sites is greatest

NicalonTM - A product of Nippon Carbon Co., Japan.

Figure 1a. Optical micrographs of CVI SiC-SiC composite prepared with uncoated Nicalon™ fibers, 500x: a) transmitted light.

Figure 1b. Optical micrographs of CVI SiC-SiC composite prepared with uncoated Nicalon™ fibers, 500x: b) reflected light.

Figure 2a. Optical micrographs of CVI SiC-SiC composite prepared with Si coated NicalonTM fibers, reflected light, a)500x.

Figure 2b. Optical micrographs of CVI SiC-SiC composite prepared with Si coated Nicalon TM fibers, reflected light, b) 2500x.

Figure 3a. Optical micrographs of CVI SiC-SiC composite prepared with Si coated Nicalon™ fibers, transmitted light, a)500x.

Figure 3b. Optical micrograph of CVI SiC-SiC composite prepared with Si coated Nicalon™ fibers, reflected light, b) 2500x.

on the Si coated fibers. Between these fan shaped growth features the SiC presumably nucleates more uniformly on the fiber surface, although detailed analysis of the nucleation process has not been conducted. The matrix is primarily β -SiC as revealed by TEM analysis, although there is evidence for some α -SiC adjacent to the SiC fibers. It is possible that the dark features shown in Figure 3b, from which the fan shaped growth nucleates, could be the alpha SiC observed in TEM but further analysis is needed to correlate the features observed in TEM with those observed in TOM.

Microstructural and microchemical characterization of fiber-matrix interfaces in two specimens of chemical vapor infiltrated (CVI) SiC reinforced with NicalonTM fibers was performed via transmission electron microscopy (TEM) with associated x-ray energy dispersive spectroscopy (EDS). One composite was reinforced with uncoated fibers and the second composite was reinforced with BN-coated fibers. The fibers were not degraded in either composite by the modest temperatures ($\approx 1000^\circ\text{C}$) incurred during infiltration and they retained their initial microstructure consisting of nanometer-size crystallites of β -SiC randomly distributed in an amorphous matrix composed of Si, C, and O (Figure 4).

In both composites, the CVI matrix was predominantly composed of randomly-oriented, densely-packed grains of β -SiC with an average diameter of ≈ 50 nm (Figures 5a&b). Microscopic porosity was not present, in contrast to the presence of large millimeter-size voids located between the fiber tows. In a few areas adjacent to either the uncoated or BN-coated fibers, the matrix consisted of columnar grains of α -SiC approximately 50 nm wide and 200 nm long (figures 6a & b). These grains were oriented with their basal (0001) planes roughly parallel to the fiber surface, giving them the appearance of having grown from the fiber surface. Beyond the length of the columnar grains the matrix consisted of small grains of β -SiC, as discussed above.

The uncoated fibers appeared to be intimately bonded to the adjacent α -SiC or β -SiC matrix; no porosity or microcracks were

Figure 4a and b. a) Bright-field micrograph of typical fiber microstructure in both composites. Mottled contrast is due to small precipitates of β -SiC in an amorphous matrix. b) Dark-field micrograph of fiber formed with diffuse ring in (c) revealing size and distribution of β -SiC precipitates.

Figures 4c and d. c) Selected area diffraction (SAD) pattern of fiber. Diffraction rings may be indexed to the cubic or β -SiC polytype. d) X-ray EDS spectrum of fiber revealing the presence of O in addition to Si and C in the fiber. The presence of Ar in the fiber is an artifact of ion milling.

Figure 5a and b. Bright-field micrograph of β -SiC matrix. Note the small grain size and absence of porosity. b) SAD ring pattern of matrix. Diffraction rings may be indexed to the cubic or β -SiC polytype.

c) EDS spectrum of the matrix revealing the presence of only Si and C in the matrix.

Figure 6a and b. a) Bright-field micrograph of interface between BN-coated fiber and adjacent α -SiC matrix. Note absence of porosity or microcracks. Linear features in a α -SiC are due to different α polytypes. b) SAD pattern of α -SiC. Rings may be indexed to hexagonal or α -SiC polytypes. Streaking is due to the presence of different α polytypes.

observed at the interface (Figure 7a). No interfacial phases or detectable amounts of chemical segregation (Figure 7b) were observed near the interface indicating that there was very little reaction between the fiber and the matrix during infiltration. However, the slightly darker contrast of the interfacial region (Figure 7a) suggests that its composition may differ slightly from that of the fibers and the matrix. A small difference in composition in a region this size could not easily be detected by EDS due to beam spreading and the fact that the probe diameter is on the order of the size of the interfacial region.

The BN-coated fibers appeared to be similarly well-bonded to the matrix (Figure 6a) and no reaction between the fiber and the matrix appears to have occurred. The BN coating could not be detected in TEM images or diffraction patterns of the interface and may have been volatilized during infiltration. However, x-ray EDS analysis (Figure 6c) revealed that a small amount of N was present at the interfaces which may be due to remnant BN or due to the incorporation of N into the amorphous phase of the fiber during volatilization of the coating. Boron from the BN coating may also be present at the interface but its detection is beyond the capability of our x-ray detector. The lighter contrast of this interfacial region suggests that it may also possess a chemical composition slightly different from that of the adjacent fiber and matrix, as discussed above.

Fracture Properties of Hot-Pressed SiC Reinforced Si_3N_4

Flexure strength and fracture resistance measurements are currently being performed at room temperature and elevated temperatures for the SiC-reinforced Si_3N_4 materials prepared at PNL. Both NicalonTM fiber and Tateho whisker materials were fabricated and tested. Four-point bend testing and chevron notch (CN) testing apparatus have been established at PNL so that mechanical properties can be accurately measured from room temperature up to 1500°C in air. These results indicate that the

Figure 6c. EDS spectrum revealing the presence of N in the fiber-matrix in (a).

Figure 7. a) Bright-field micrograph of interface between uncoated fiber and β -SiC matrix. Note absence of porosity or microcracks. b) EDS spectrum of interface revealing presence of only Si, C, and O.

unreinforced, hot pressed Si_3N_4 material has good strength and toughness while the composite materials have comparatively lower strengths. The whisker reinforced material exhibited a small increase in toughness over the HPSN Si_3N_4 while the fiber reinforced materials had lower toughness.

Test Apparatus

A SiC four-point bend fixture is being used for the flexure strength and toughness measurements. This fixture accommodates a rectangular specimen geometry of between 45 and 60 mm long with a width of 4 mm or less. The specimen height (thickness) can be within the range of 2 to 6 mm. An inner loading span of 2.000 +/- .001 cm and outer span of 4.002 +/- .001 cm are provided by the fixture. Specimen loading is partially articulated by SiC roller pins and a SiC ball on a plunger. The fixture is capable of 1500°C operation since both pushrod and supports are SiC. It is currently being used with a CM, Inc. MoSi_2 -element furnace capable of 1700°C operation.

Loading is accomplished by an Instron load frame equipped with a 500 kg tension-compression load cell. Load-displacement data are generated by measuring load as a function of crosshead displacement. Both the four-point bend and CN test require only the load at failure in order to calculate strengths and fracture toughness.

Fracture Strength Testing

Rectangular test bars are machined from hot-pressed disks (7.62 cm x 0.6 cm) using standard diamond grinding and polishing operations. Typical dimensions are 50.8 mm x 3.6 mm x 2.7 mm, with surface finishes typically 7 μm or better. Testing is performed using a crosshead speed of 5.08×10^{-3} in/min and recording the load at specimen failure. The specimens are oriented so that crack propagation is transverse to the plane of the hot-pressed disk. Fracture strengths for unreinforced and fiber and whisker

reinforced HPSN are shown in Figure 8. Room temperature fracture strengths of both the whisker and fiber reinforced material are less than the unreinforced material with strengths of 306 MPa for the whisker reinforced, 250 MPa and 323 MPa for the dry-blended and ball-milled (square points) fiber reinforced material, respectively, and 701 MPa for the unreinforced material. One explanation for the lower fracture strengths in the reinforced material might be the presence of internal microcracks resulting from whisker and fiber agglomerates and a difference in the α/β Si_3N_4 ratio for reinforced relative to unreinforced material. Evidence for crack initiation at whisker and fiber agglomerates was presented previously (5). Ball-milling is expected to be more efficient at breaking up fiber agglomerates than is dry-blending, so the higher fracture strength of the ball-milled material relative to the dry blended material may also have resulted from fewer fiber agglomerates. A higher α/β ratio has been reported previously (6) for the composite materials relative to HPSN and since high fracture strength of Si_3N_4 is associated with low α/β ratios, the lower fracture strengths of the composite materials may be associated with the observed change in the α/β ratio.

Fracture strengths of the fiber and whisker reinforced material at 1000° and 1200°C are also shown in Figure 5. The whisker reinforced material exhibited a slight increase in fracture strength at 1000°C relative to 25°C and then a decrease at 1200°C relative to 1000°C. The fiber reinforced HPSN produced by dry-blending (square points) also exhibited an increase in fracture strength at 1000°C relative to 25°C as did the whisker reinforced material; however, the fiber reinforced material produced by ball-milling (up-right triangles) did not. A decrease in the fracture strength at 1200°C relative to 1000°C also occurred with the fiber reinforced material as with the whisker reinforced material. The decrease in the fracture strength at 1200°C in both materials is thought to be due to the softening of the MgO rich glass phase in the grain boundaries of the Si_3N_4 .

Figure 8. Four-point bend fracture strength of whisker and fiber reinforced HPSN at temperatures of 25° to 1000°C.

Fracture Toughness

A four-point loaded chevron notch (CN) specimen has been designed for fracture resistance and work of fracture studies. Preliminary results indicate that this specimen design is suitable for accurate fracture toughness (K_{IC}) data and for work of fracture determinations at room temperature, as well as at elevated temperatures. CN testing has advantages for fracture mechanics testing of brittle materials since initial crack propagation is stable, R-curve behavior can be observed if it exists, the specimen is simple to machine, and it gives accurate work of fracture data. However, it only has accurate fracture mechanics solutions for restricted ranges of specimen geometries.

A CN specimen was designed based on the four-point bend bar specimen developed earlier. A stress intensity factor was chosen such that the measured K_{IC} is calculated from:

$$K_{IC} = \frac{P_{max}}{B\sqrt{W}} F_m^*$$

where P_{max} is the maximum load at failure, B is the specimen width, W is the specimen height across the loading pins, and F_m^* is the geometry factor. A value of $F_m^* = 15.9$ was determined by choosing $K_{IC} = 6.0 \text{ MPa}\sqrt{\text{m}}$ for the unreinforced Si_3N_4 . It is important to note that for any choice of F_m^* that the toughness determinations are accurate in a relative sense. A method for calculating F_m^* is available and a calculated value will be reported later.

Fracture toughness values for unreinforced and fiber and whisker reinforced HPSN are shown in Figure 9. Room temperature fracture toughness for the whisker reinforced HPSN material was about 30% greater than the unreinforced material while the fracture toughness values for the fiber reinforced material was less. The improved fracture toughness of the whisker reinforced material is not associated with whisker pull-out as the whisker-matrix interface contained a thin glass layer, as reported previously (5),

Figure 9. Chevron-notch fracture toughness of whisker and fiber reinforced HPSN at temperatures of 25° to 1200°C.

which is expected to form a strong whisker-matrix bond. Also, there was no evidence of matrix microcracking or fiber pull-out events increasing the work of fracture on the load-deflection curves (5). A possible source of the increased toughness is that the whisker reinforced composite has a higher intrinsic fracture strength than the matrix because of the high strength whisker reinforcement. A higher intrinsic fracture strength requires a high stress at the tip of a given notch or flaw to produce unstable flaw growth. The flat flexure samples do not determine the intrinsic fracture strength as they reflect the stress needed to produce unstable flaw growth from internal flaws of unknown and variable dimensions. Therefore, even though the fracture strength of the whisker reinforced HPSN was less than that of the unreinforced HPSN, the intrinsic fracture strength could possibly be greater because the composite materials have larger internal flaws. As discussed previously, fracture of the composite materials initiated at whisker agglomerates which were porous, low strength regions within the material.

The fracture toughness of the unreinforced HPSN material was similar at 1000°C and 25°C while the whisker reinforced material exhibited a decrease at 1000°C relative to 25°C and an increase at 1200°C relative to 1000°C. The fracture toughness values show an inverse relationship to the fracture strength values with the higher strengths at 1000°C corresponding to a lower toughness. However, at most, only 2 samples were tested so these trends may only reflect scatter in the data which may not be evident with test results from a large number of samples.

Hot Salt Corrosion of Hot-Pressed SiC Reinforced Si₃N₄

A schematic drawing showing potential reactions in a ceramic composite are given in Figure 10 with comparison to a monolithic Si₃N₄ material. In a ceramic composite which exhibits fiber or whisker pull-out or crack bridging for toughening, the fibers or whiskers are exposed to the environment while with metal matrix

Monolithic Si₃N₄ **SiC-Whisker Reinforced Si₃N₄ Composite** **Rate Processes**

- 1) O₂ transport to film
- 2) Oxidation process of matrix and whiskers
- 3) Deformation rate of film at crack-tip
- 4) Deformation rate of film at matrix-whisker interface

Figure 10. Schematic showing potential crack tip reactions involved in environment-induced crack growth of monolithic and composite ceramics.

composites the fibers and whiskers fail ahead of the crack tip because of extensive plasticity. Several environment-materials reactions are possible with a ceramic matrix composite including reaction with: 1) the glass phase in the grain boundary; 2) the fibers or whiskers and; 3) the interface between the fibers/whiskers and the matrix. Presuming that the grain boundary chemistry of the matrix in a composite material is similar to the monolithic material, reaction rates with the grain boundaries can be estimated from monolithic materials. Also, information on reaction rates with the reinforcing phase, i.e. SiC, may be useful for estimating the reaction rate of the exposed fibers and whiskers. This is especially true for crystalline, SiC; however NicalonTM fibers are not stoichiometric nor are they chemically stable. Johnson et al. (7) evaluated the decomposition of several SiC fibers and found SiO and CO vaporization at temperatures ranging from 1000° to 1400°C. These results indicate that there is excess C and O in these fibers and that chemical reaction rate data for stoichiometric SiC would not properly predict their reaction rates with the environment.

Reaction rates with the interface between the fibers or whiskers and the matrix are essentially unpredictable from bulk chemical reaction rate data. The interface controls the fracture strength and toughness and the creep rate so that any reaction with the environment will alter the near crack tip properties of the material. The interfacial chemistry and structure in ceramic composites vary from clean-atomically bonded to an interface with a relatively thick layer applied as a coating to the fiber or whisker. Examples of coatings include carbon, BN, and SiO₂.

Lin et al. (8) conducted oxidation studies of SiC reinforced Al₂O₃ and reported that oxidation in the composite occurs by a series of reactions which involves the oxidation of the SiC whisker to form a silica glass and graphitic carbon. The silica glass penetrated the Al₂O₃ and Lin et al. reported that oxidation in the composite occurred by a series of reactions which involves the

oxidation of the SiC whisker to form a silica glass and graphite boundaries to form mullite. A whisker free layer of mullite and silica glass is formed on the surface. It was also demonstrated that the mullite reaction layer contributed to crack initiation of the composite under cyclic compressive loads. The oxidation study by Lin et al. demonstrates a potential corrosion reaction in other ceramic composites.

Corrosion tests were performed on unreinforced and SiC whisker and fiber reinforced HPSN in molten 100% Na_2SO_4 salt. The materials evaluated were those prepared at PNL by hot pressing and described in previous reports (5, 6, and 9). Tests were performed at 900°C to 1000°C for a single time of 8 hours with heating done in an electric resistance furnace. The samples and salt were held in a platinum crucible during the corrosion exposure. The salt was removed by immersing the sample in a hot water-ultrasonic bath while the underlying glass layer was removed by immersion in HF. The sample dimensions and weight were determined prior to the corrosion exposure and the weights determined following exposure and cleaning. The surfaces of the samples were examined by scanning electron microscopy (SEM) following weighing. Samples were coated with gold to minimize charging in the microscope.

Weight loss values for unreinforced, whisker and fiber reinforced HPSN at temperatures of 900° to 1000°C are given in Table 1. Weight loss values were only around 1% or less following

Table 1. Molten Salt Corrosion of SiC Reinforced HPSN

<u>Weight Percent Loss in Na_2SO_4</u>				
<u>Temp°C</u>	<u>Si_3N_4 Matrix</u>	<u>Nicalon™ Fiber Reinforced Dry Blended</u>	<u>Nicalon™ Fiber Reinforced Ball-Milled</u>	<u>Whisker Reinforced</u>
900	0.15	1.15	1.32	0.87
950	0.26	1.99	1.76	0.10
1000	21.66	58.62	59.84	28.71

8 hours at 900°C while the Nicalon™ fiber reinforced HPSN exhibited an increased weight loss to about 2% at 950°C and 60% at 1000°C. In general, the unreinforced and whisker reinforced material exhibited equal weight losses. The slightly higher weight loss values for the whisker reinforced material relative to the unreinforced material is probably within the accuracy of the weight loss measurements considering that it was necessary to immerse the samples in HF to remove the glass layer.

SEM evaluation of the samples revealed that the large weight loss of the Nicalon™ fiber reinforced material resulted from preferential corrosion of the SiC fiber, Figure 11. Preferential SiC fiber corrosion is evident at 950° and 1000°C even though the corrosion rate at 950°C was minimal. The unreinforced and SiC whisker reinforced material show surface structures typical of etched Si_3N_4 with removal of the grain boundary glass phase revealing the β acicular Si_3N_4 . There was no evidence that the crystalline SiC whiskers were preferentially corroded, Figure 12.

Comparison of the present results to those reported by Tressler et al. (10), on molten salt corrosion of SiC and Si_3N_4 indicates that the HPSN material prepared with MgO additive was less stable in 100% Na_2SO_4 at 1000°C than the commercially available material used in their test. Tressler reported only a small or negligible weight change after 8 hours at 1000°C with a more significant change occurring following 40 hours. In contrast, a 20% change was observed in the present study after 8 hours at 1000°C. Tressler reported a large weight change for both reaction sintered and hot-pressed SiC. This is in contrast to the apparently little corrosion observed for the crystalline single crystal SiC whiskers in the whisker reinforced composite material. Possibly, the molten salt is reacting primarily with the grain boundary glass phase in the polycrystalline SiC examined by Tressler.

Figure 11a and b. Scanning electron micrographs on the surface of HPSN immersed in molten Na_2SO_4 for 8 hours at 950°C , a,b) NicalonTM fiber reinforced HPSN.

Figure 11c and d. Scanning electron micrographs of the surface of HPSN immersed in molten Na_2SO_4 for 8 hours at 950°C , c) HPSN without reinforcement, and d) Tatehc whisker reinforced HPSN.

Figure 12. Scanning electron micrograph of the surface of Tateho whisker reinforced HPSN immersed in molten Na_2SO_4 for 8 hours at 950°C .

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PNL-1(A) - EVALUATION OF CANDIDATE MATERIALS FOR SOLID OXIDE FUEL CELLS

J. L. Bates, W. J. Weber and L. A. Chick

Pacific Northwest Laboratory
Post Office Box 999
Richland, Washington 99352

INTRODUCTION

The purpose of this work is: (1) to identify, develop, and demonstrate advanced new materials for use as alternative electrodes and current interconnections for improving the performance, reliability, and efficiency of solid oxide fuel cells (SOFC), and (2) to develop an understanding of synergistic effects of materials properties, structures and compositions on the electrochemical processes for high-temperature, solid electrolyte and electrode materials in electrochemical cells.

Background

Fuel cells are emerging as an attractive, clean and efficient technology for the direct conversion of fossil fuel to electrical energy. High-temperature solid oxide fuel cells (SOFC) have seen promising major advancements in recent years with long-term and multiple kilowatt testing.

State-of-the-art SOFC concepts are based on a Y_2O_3 stabilized ZrO_2 electrolyte with a $La(Sr)MnO_3$ air electrode, a $ZrO_2/Ni(Co)$ cermet fuel electrode, and $La(M_2)CrO_3$ as the current interconnection. As a result of materials interactions, incompatible electrical/polarization interface characteristics, and the complex series of fabrication/processing steps required in present designs, these current materials are not meeting the design and performance requirement placed on them in state-of-the-art SOFC concepts. Although design changes and improved fabrication techniques may help control some of the problems,

the ultimate success of SOFC technology will require alternative electrode and interconnection materials to eliminate or minimize present limitations. Improved fuel cell performance is possible as new, alternative materials are developed that allow simple, conventional fabrication methods to be utilized, resulting in lower costs and improved performance. New alternative materials with improved properties obtained through an understanding of the electrochemical processes associated with the electrochemical cells, such as SOFC, are the major keys to the broader application, improved performance and better economics of high-temperature, solid electrolyte technology.

Approach

The scope of this investigation is to synthesize new materials, determine electrical transport properties, evaluate thermal and electrochemical compatibility with other SOFC materials, and obtain an understanding of the effects of structure, microstructure, phase equilibria, oxygen partial pressure, and additives on these properties.

New analytical techniques using complex impedance being developed will be coupled with conventional electrochemical methods to study the electrochemical processes and behavior of materials for solid oxide fuel cells and other high-temperature, electrolyte electrochemical cells.

This study of materials and electrochemical processes emphasizes:

- (1) Mixed ionic-electronic conducting oxides of $ZrO_2(HfO_2)-RE_xO_y-MO_2$ systems as advanced, potential electrode materials to promote enhanced electrode/electrolyte charge transfer and easier SOFC fabrication processes;
- (2) Complex $Y(M')(Cr,M'')O_3$ and $La(M')(Cr,M'')O_3$ as electronically conducting current interconnections with improved compositions, improved thermal compatibility, higher electrical conductivity and enhanced air sinterability for ease of fabrication.

DISCUSSION OF CURRENT ACTIVITIES

Electrode Materials

The anode or fuel electrode of the solid oxide fuel cell operates at very low oxygen partial pressures. Present state-of-the-art SOFC anodes are porous Ni/Y₂O₃ stabilized ZrO₂ composites bonded to the Y₂O₃ stabilized ZrO₂ electrolyte. However, because of inherent differences in the thermal expansion coefficients of metals and the oxide electrolyte, it is advantageous to replace the metal with a more compatible, all ceramic electrode with properties that better match the electrolyte. The approach in this study is to study oxides which become high-electronic conductors in the partially reduced or substoichiometric state. Two oxide systems are being evaluated, ZrO₂-Y₂O₃-TiO₂ and ZrO₂-Y₂O₃-CeO₂.

ZrO₂-Y₂O₃-CeO₂ System

Compounds in the ZrO₂-Y₂O₃-TiO₂ system were prepared by coprecipitation of powders from a solution of zirconium, yttrium and titanium sulfates. The precipitated powders were filtered, washed, dried, and calcined before being pressed into bars and sintered. Electrical conductivities were measured in air and in 4% hydrogen - 96% argon mixture using a four-probe technique with platinum knife-edge contacts.

The electrical conductivity of (0.9-x)ZrO₂·xCeO₂·0.1Y₂O₃ with x varying from 0.0 to 0.9 was measured in air at atmospheric pressure from 625 to 1600 K. The electrical conductivity decreased with increasing CeO₂, reaching a minimum between x = 0.45 and 0.65, Figure 1. The electrical conductivity then increased with higher CeO₂ content with the 90 mole% CeO₂ (x = 0.9) higher than the ceria-free, 10 mole% Y₂O₃ stabilized ZrO₂. The activation energies were 0.96, 1.2, 1.36, 1.38, and 0.83 eV for x = 0.0, 0.25, 0.45, 0.65 and 0.9, respectively.

Figure 1. Electrical Conductivity ($\log \sigma T$ vs $1/T$) of $(0.9-x)\text{ZrO}_2-x\text{CeO}_2-0.1\text{Y}_2\text{O}_3$ in Air.

The magnitude of the electrical conductivity for the $0.1\text{Y}_2\text{O}_3 \cdot 0.9\text{ZrO}_2$ is slightly lower than that for a $0.094\text{Y}_2\text{O}_3$ stabilized ZrO_2 single crystal but with a similar activation energy. (1) These differences are typical of the Y_2O_3 stabilized ZrO_2 ionic conductors with electrical conductivities of the fluorite phase decreasing as the concentration of the stabilizing agent is increased above the minimum content required for stabilization of the fluorite, fcc lattice. Similar results were observed for the $x = 0.25$ $\text{CeO}_2\text{-Y}_2\text{O}_3\text{-ZrO}_2$ composition which has a higher stabilizing CeO_2 plus Y_2O_3 content but is still fcc fluorite.

The gradual decrease in conductivity, the minimum and the following increase with increasing CeO_2 content coupled with the gradual increase of the activation energy, the maximum between 45 and 65 mol% CeO_2 and the decrease at high CeO_2 content, support the reported single phase, fcc fluorite solid solution for all compositions of

$(0.9-x)\text{ZrO}_2 \cdot x\text{CeO}_2 \cdot 0.1\text{Y}_2\text{O}_3$ as reported by Cales (1). The presence of the 10 mol% Y_2O_3 appears sufficient to fully alter the reported two-phase tetragonal-cubic structure between 18 and 80 mol% CeO_2 at high-temperatures of the CeO_2 - ZrO_2 phase diagram, Tani, et. al., (4).

The electrical conductivity data also agree well with other reported values of similar oxide compositions. The electrical conductivity of the 10 mole% CeO_2 is slightly lower than that measured for single crystal $0.094\text{Y}_2\text{O}_3$ - 0.906ZrO_2 measured at this laboratory (1). It is between 20 and 25% higher than that reported by Cales (2) in his study of the ZrO_2 - CeO_2 - Y_2O_3 system. The variation in conductivity with increasing CeO_2 content up to $x = 0.65$ is similar to that reported by Cales (2) who did not make measurement to high values of x .

Measurements under highly-reducing conditions were initiated for 0.9CeO_2 - $0.1\text{Y}_2\text{O}_3$, ZrO_2 -free in 96% argon-4% hydrogen. The electrical conductivity increases by 1 to 2.5 orders of magnitude (0.1 to 1.9 mho/cm at 1273 K) with a decrease in activation energy (0.81 to 0.56 eV), Figure 2. The significant conclusion from these limited data is that the ionically conducting CeO_2 doped with Y_2O_3 in air exhibits an increase in electrical conductivity with the increase assumed to result from an increased electronic conduction. These data are also consistent with other reported values for $0.1\text{Y}_2\text{O}_3$ doped (2) and 0.1ZrO_2 doped (3) CeO_2 compositions in reducing atmosphere.

Interconnect Materials

The novel approach for the synthesis of air-sinterable, active $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$ powders as described in the last report (5) has been applied to the production of submicrometer $\text{La}(\text{M}')(\text{Cr},\text{M}'')\text{O}_3$ powders. $\text{La}(\text{Sr})\text{Cr}(\text{M}')\text{O}_3$ and $\text{Y}(\text{M}')(\text{Cr},\text{M}'')\text{O}_3$ systems are being studied as current interconnections for SOFC because of the potential for modifying (increasing) the thermal expansion while retaining or increasing the high electrical conductivity of the presently used $\text{La}(\text{Sr})\text{CrO}_3$ and $\text{La}(\text{Mg})\text{CrO}_3$. This synthesis technique, although still being developed, has produced homogeneous, submicrometer powders between 0.1 and 0.7 μm

Figure 2. Electrical conductivity (Log σT vs $1/T$) of $0.9\text{CeO}_2\text{-}0.1\text{Y}_2\text{O}_3$ in Air and 4% Hydrogen-96% Argon.

of chromite powders which have produced high air-sintered densities of La(M)CrO_3 . (1) The major difficulty encountered in the process is the formation of significant amounts of agglomerates approximately $1\text{ }\mu\text{m}$ in diameter which cannot be broken-up by sonification and which appear to limit higher air-sintered densities.

The process was used to synthesize La(Sr)Cr(Al)O_3 powders for sintering samples for the study of the electrical and thermal properties of these complex chromites. Powders with varied amounts of Al substituted for Cr were prepared. The characteristics of the powders were similar to those of the aluminum-free La(Sr)CrO_3 . However, the addition of Al appears to reduce the air sinterability of the chromite powders with the sintered density decreasing with increasing Al content. The chromites with greater than 0.1 mole percent Al also tended to fracture on sintering and to warp when sintered on an aluminum oxide support.

Electrochemical Processes

The electrochemical processes in solid oxide fuel cells are critical to performance. It is important that these processes be understood and used to evaluate the materials, materials interactions and material interfaces and possible degrading effects of current, temperature and time. Impedance measurement is being used to investigate the transport phenomenon in solid electrolyte, high-electronically nonmetallic conductors and interfacial conduction and charge transfer behavior. The technique measures the resistance and capacitance of materials, interfaces and cells over a wide range of frequency. An impedance or admittance plot is constructed which can provide, when properly analyzed, significantly more information than a dc or single frequency ac electrical measurement and or conventional electrochemical polarization measurement. The method has the potential for separating a number of electrochemical and electrical processes: (1) charge separation in the bulk, (2) charge transfer at the electrode/electrolyte interface, (3) absorption reactions, (4) generation and recombination and (5) diffusion. Thus, it can be used to study the ionic and electronic conductivity in the bulk grains, the grain boundaries as well as determining the processes at the electrode/electrolyte interfaces and surfaces that are so critical in high-temperature electrolyte cells.

An impedance spectroscopic system has been assembled and a test cell using disc samples constructed. An initial study was made of the electrical properties of a reference, sintered 9.4 mol% Y_2O_3 stabilized ZrO_2 . The impedance spectroscopy system consists of an automated control and data acquisition system using a high-frequency response analyzer at frequencies from 10 μHz to 20 MHz and two equivalent circuit routines for data analysis. A schematic of the impedance system is shown in Figure 3. The two impedance fitting programs are being used to fit and analyze the complex curves observed during impedance measurement.

Figure 3. The Schematic of the Complex Impedance Spectroscopic System.

(1). "LOMFP" ("LEVM" - "OLSON"), developed by J. Ross MacDonald of the University of North Carolina, Chapel Hill, NC., is a collection of individual programs for complex nonlinear least squares fitting. LEVM is extremely fast and will find optimum parameter values for far-removed assumed spectra. OLSON is not as good at converging, but fed output from LEVM will be more likely to locate an absolute value. The two are generally run in tandem. This is an advanced method and when used with known responses is flexible and will be important in the study of interfacial phenomena.

(2). "EQUIVCRT", developed by Bernard A. Boukamp, University of Twente, Enschede, The Netherlands, is a menu-driven combination of three major subprograms which enable the decomposition of a dispersion spectrum into sub-circuit components, their nonlinear least squares fitting (NLLS-fitting) and subtraction from the overall spectrum and final NLLS-fitting of the overall spectrum. This program is user-friendly with excellent documentation. "EQUIVCRT" is an excellent tool for analyzing all but the most

special cases of imittance spectra, such as for electrical properties of bulk ceramics.

The technique was used to determine the electrical characteristics of a sintered $0.094\text{Y}_2\text{O}_3 \cdot 0.906\text{ZrO}_2$ solid electrolyte with fired platinum-paste electrodes. An example of the complex impedance spectrum for this electrolyte at 623 K in air is shown in Figure 4. It illustrates the separation of the grain and grain boundary conduction and the blocking effect at the interface between the platinum electrode and the sample surface. The electrical conductivity of the grains, grain boundary and Ft - $0.094\text{Y}_2\text{O}_3 \cdot 0.906\text{ZrO}_2$ interface as a function of temperature is illustrated in Figure 5. The slope for the interface is very similar to the conductivities for the grain and grain boundary. This was not expected and is being studied further.

Figure 4. The Impedance Spectrum of Sintered $0.906\text{ZrO}_2\text{-}0.094\text{Y}_2\text{O}_3$ at 623 K.

Figure 5. The Grain and Grain Boundary Electrical Conductivity ($\log \sigma$ vs $1/T$) in Air for Sintered Face-Centered Stabilized $0.906\text{ZrO}_2\text{-}0.094\text{Y}_2\text{O}_3$, and for Oxide-Platinum Interface.

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SNL-1 - CERAMIC CATALYST MATERIALS: HYDROUS METAL OXIDE
ION-EXCHANGE SUPPORTS FOR DIRECT COAL LIQUEFACTION

C. H. F. Peden, B. C. Bunker and S. L. Martinez

Sandia National Laboratories
Inorganic Materials Chemistry Division
Albuquerque, New Mexico 87185-5800

INTRODUCTION

Coal is our most abundant fossil fuel energy source. However, it requires extensive chemical treatment and processing to convert it from a hydrogen-poor "dirty" solid to a "clean" premium liquid fuel such as gasoline. One of the missions of the Department of Energy's AR&TD research is to permit expanded use of coal-based systems by providing a focus for the exploration of ideas pertaining to coal science, conversion and utilization. This project seeks to accomplish that mission by exploring the synthesis and evaluation of new ceramic catalytic materials for efficient, direct conversion of coal to clean liquid fuels. Because the recoverable U.S. supplies of coal are 50 to 100 times that of crude oil, development of new catalysts for efficient conversion of coal to environmentally acceptable liquid fuels would have an enormous impact on extending our useable energy reserves.

As an AR&TD project, the focus of this program is to conduct research and development on catalytic materials for fossil energy applications. In this way, we are obtaining a better understanding of these materials that will impact the long-term, generic needs of various fossil fuel technologies. However, sufficient testing of the hydrous metal oxide ion-exchange catalysts with coal and coal-derived feeds has been accomplished to demonstrate that they show great promise for end-use process applications.¹

The specific materials under study in this AR&TD project are from a group of hydrous oxide ion-exchange compounds of Ti, Zr, Nb, and Ta developed at Sandia National Laboratories. These compounds have been used to prepare catalysts by a novel synthesis route involving the incorporation of active metals by ion exchange.² Hydrous oxide ion-exchange compounds were originally developed at Sandia for use in the decontamination of aqueous nuclear waste and as precursors for ceramic materials.³ The use of these compounds as ceramic catalyst supports arises from the unique properties which these systems exhibit: 1) any metal, or mixture of metals, can be incorporated into the materials over a wide concentration range by a simple process; 2) the materials have high surface area which displays a unique temperature dependence (increasing with increasing T); 3) they exhibit good chemical stability; 4) solution chemistry or more conventional high temperature reactions can be used to provide control of the active metal oxidation state; 5) acidity and basicity of the substrate can be modified by ion exchange; and 6) the catalysts can be prepared on transition metal-oxide supports (Ti, Nb, and Ta) known to undergo a so-called "strong metal-support interaction" (SMSI).

The hydrous metal oxides investigated in this study belong to a group of inorganic ion-exchange compounds that can be represented by the empirical formula $M(M'_xO_yH_z)_n$, where M is an exchangeable cation and M' is Ti, Nb, Zr, or Ta. When added to a solution of aqueous metal cations, these powdered materials will react to form amorphous precipitates containing the dissolved metal which has replaced the exchangeable cation, M. Catalytic activity has been measured at Sandia for materials synthesized in this manner.^{1,4} For example, catalysts prepared using the hydrous titania ion exchangers, even at low active metal loadings of 1%, are equally effective for conversion of coal to low molecular weight products as a commercial Ni-Mo/alumina catalyst containing 15% by weight active metals.¹

One possible reason for the improved performance of the catalysts prepared from the hydrous titanate materials may be that active metals are dispersed more completely via the ion-exchange process than when

loaded by traditional incipient wetness techniques. As such, these materials offer a method to prepare greatly improved heterogeneous catalysts for many applications, provided we understand the important variables in the synthesis.

Our goal is to develop a fundamental understanding of the preparation and properties of these unique materials. Specifically, we will investigate the following areas:

- 1) molecular and extended macroscopic structure of the hydrous titanate,
- 2) mechanism of incorporation of catalytic metals, and
- 3) catalytic and reactivity studies of the metal loaded catalysts.

Having developed this basic understanding, we envision being able to tailor catalyst properties for specific applications, as well as providing foundation for further catalyst development.

DISCUSSION OF CURRENT ACTIVITIES

During this reporting period, we have continued our studies of the molecular structure of the catalyst support by obtaining ^{17}O solid state nuclear magnetic resonance (NMR) and Raman spectra of several crystalline model titanate compounds in order to unambiguously assign the features observed in the spectra we have previously obtained of the powdered, amorphous sodium titanate materials. Because ion-exchange processes play a key role in active metal loading, an understanding of molecular structure, and correlated measurements of the acid/base and ion-exchange properties of the hydrous titanates,⁵⁻⁷ is crucial for the determination of catalyst metal adsorption mechanisms. Unfortunately, the molecular structure and ion-exchange site distribution in hydrous sodium titanate cannot be determined using X-ray crystallography because the material is amorphous. Instead, the molecular structure is inferred from the results of several spectroscopic techniques, each of which is sensitive to different structural features. These studies are expected to be completed during the next six months and so will be described in detail in the next semiannual report. Studies to determine the

mechanism(s) by which catalytically active metals are adsorbed by sodium titanate supports were continued this reporting period.⁸ Three nickel catalysts were prepared under different solution conditions which we predicted to have dramatically different structural and catalytic properties. To test this, we have characterized the catalysts by solution analyses, by transmission electron microscopy (TEM), and by measuring the activity and selectivity of the catalysts for a known "structure sensitive" reaction, the hydrogenolysis of n-butane. In this report, we detail the results of this work. Finally, we have initiated studies of the loading of active metals which exist as anions in solution, taking advantage of the ability of the titanates to function as anion as well as cation exchangers. We report some of the initial results of these studies here

Experimental

Hydrous sodium titanate samples were prepared using the method of Dosch and Stevens.² Titanium isopropoxide was slowly added to a 15 wt% solution of sodium hydroxide in methanol. The resulting solution was hydrolyzed by the addition to 10 vol% water in acetone. For NMR experiments, oxygen-17 labeled samples were prepared by carrying out the hydrolysis with $H_2^{17}O$. The hydrolysis product is an amorphous, white precipitate which contains, after vacuum drying at room temperature, approximately 13.5 wt% water and 2.5 wt% residual alcohol. The ion-exchange characteristics of the sodium titanate and the hydrolysis behavior of the nickel nitrate solutions were characterized using a combination of potentiometric titrations, ICP analysis of filtrates, and surface charge measurements obtained using a Matec electrosonic amplitude device.

Three different nickel-loaded sodium titanates were prepared by exposing 5 gm of the sodium titanate powder to aqueous solutions of nickel nitrate containing sufficient nickel to incorporate one equivalent of nickel for every two equivalents of sodium on the support (corresponding to the stoichiometry associated with complete ion

exchange). Each sample was prepared using different pH conditions (and thus, different Ni(II) concentrations) to vary the mechanism of nickel loading (see Results and Discussion). To obtain atomic dispersions of nickel via ion exchange, the titanate powder was added to pH 5-6 solutions of aqueous $\text{Ni}(\text{NO}_3)_2$. This procedure was performed three times with intermediate filtrations. To favor the formation of small, hydrolyzed clusters, a stoichiometric nickel solution was added dropwise to a slurry of the titanate powder in deionized water at a pH of 11. Concurrent with the Ni addition, NaOH was added to maintain the pH at or near 11. To favor the formation and adsorption of colloidal nickel hydroxide, sodium hydroxide was used to adjust the pH of the nickel nitrate solution to pH 12.7 prior to the addition of the sodium titanate. The pH adjustment caused the dissolved nickel to form a colloidal suspension of nickel hydroxide which was then adsorbed on the sodium titanate support. All three samples were analyzed for Na, Ni, and Ti by redissolving the titanate powders in strong acid and analyzing the solutions using atomic adsorption and inductively coupled emission spectroscopies.

Transmission electron micrographs were obtained from either a JEM 200CX instrument or a JEOL 2000FX TEM/STEM using low beam intensity to avoid beam alteration of the samples. The powders were supported on holey carbon films mounted on copper grids. Powder surface areas were measured using N_2 adsorption in a Micromeritics Digisorb 2600 analyzer. The samples were outgassed at 150 °C for 4 hours in flowing He before taking the measurements. Metal surface area was determined by static volumetric chemisorption using research purity gases obtained from Matheson. The chemisorption was performed at room temperature and total uptake of H_2 was used as a measure of the surface concentration of Ni. All catalysts had a nominal loading of 10-11% Ni. The catalytic activity for n-butane hydrogenolysis was measured using a feed stream containing H_2 and n- C_4H_{10} in the ratio 20:1 at a total pressure of 101.4 kPa. Rates are reported as a turnover frequency (TOF), or the number of n-butane molecules reacted per second per surface Ni atom, with the latter quantity being determined by H_2 chemisorption.

Results and Discussion

To optimize the use of the amorphous sodium titanate powders as catalyst substrates, it is important to fully characterize the ion-exchange properties of the material. Further, the solution properties of the active metal to be loaded onto the support will be an important parameter in the control of the adsorption process. For example, exposure of sodium titanate to a nickel salt solution does not guarantee that nickel will be loaded onto the sodium titanate, or that the nickel, if loaded, will be dispersed on an atomic level. Sodium titanate only behaves as a cation exchange material under certain pH conditions. The solution pH also influences the hydrolysis and speciation of dissolved nickel ions,⁹ which can form large polymeric clusters or colloidal particles which are not adsorbed by the sodium titanate via a simple ion-exchange process. Thus, in order to control the mechanism by which nickel is loaded onto sodium titanate and to control the degree of nickel dispersion, we need to understand the ion-exchange properties of the sodium titanate support, the hydrolysis chemistry of the dissolved nickel, and how the different nickel species are expected to interact with the titanate support.

I. Ion-Exchange Behavior of Sodium Titanate

The ion-exchange characteristics of sodium titanate supports are summarized in Fig. 1 (4). In the figure, proton (H^+) consumption is plotted by the solid line as the $Na_{0.5}Ti$ is titrated from a basic pH (~ 12) with HCl. Na^+ (+) loss from and Cl^- (-) adsorption onto the support are followed by analysis of the solutions by ICP. At pH values above the isoelectric point (iep) of sodium titanate (pH 5), the surfaces of the sodium titanate particles are covered with anionic surface sites that are charge compensated by cations such as sodium. Above pH 5, the titanate support can function as a cation exchanger. For example if $Ca(II)$ ions are added to a sodium titanate slurry, solution analyses indicate that one calcium ion is adsorbed by the

Figure 1: Plot of the H^+ (solid line) and Cl^- (-) consumption from solution, and Na^+ (+) depletion from a $\text{Na}_{0.5}\text{Ti}$ during titration with HCl (starting pH = 12). Adapted from Reference 2.

support for every two sodium ions released into solution. Below pH 5, surface sites on the titanate support are primarily cationic, and the support behaves as an anion rather than a cation exchanger. In the above example, neither Ca(II) or Na(I) ions are adsorbed by the titanate powder when the solution pH is highly acidic (below pH 4). Therefore, the solution chemistry of sodium titanate suggests that if the powder is exposed to Ni(II) , and if the Ni(II) is to be loaded via an ion-exchange process, no Ni(II) adsorption is to be expected below pH 5.

Also apparent in Fig. 1 (note the two regimes of H^+ consumption at nearly constant pH of about 8 and 12) and in surface charge measurements as a function of pH (Fig. 2) is the presence of at least two anionic surface sites above pH 5. The distribution of these two sites is controllable during the synthesis of the sodium titanate powder. Using Raman and solid state ^{17}O NMR spectroscopies⁵⁻⁷ we are attempting to identify specific adsorption sites responsible for the differing solution behavior, and to characterize changes in the distribution of such site. In this way, the tailoring of the support's ion-exchange properties can be realized. In our other work⁵⁻⁷ we have also found that irreversible changes in the titanate support structure and correspondingly in the type and number of ion-exchange sites can occur during ion exchange depending on the solution pH. This result demonstrates another important consideration in the use of these materials for catalyst supports.

Figure 2: Surface charge on a calcium titanate powder in solution, measured by electrosonic amplitude (ESA), as a function of pH during a titration with HCl. The two inflection points in the curves at $\approx$ pH 7 and 10 indicate the presence of two anionic sites available for ion-exchange of cations from solution. The different curve obtained when the slurry containing the titanate powder is back-titrated from low to high pH has been discussed in previous reports.^{5,6}

II. Ni(II) Hydrolysis Chemistry

Although Ni(II) exists in solution as a simple aquated cation in acidic solutions, increases in the solution pH can lead to the deprotonation of bound water molecules, leading to hydrolysis and condensation of Ni(II) to form polymeric clusters. The calculated hydrolysis diagram⁹ for Ni(II) (Fig. 3), shows that for a 3×10^{-2} M nickel nitrate solution, hydrolysis and condensation commence at a pH of 6.5. This is evidenced by the coincidence of the calculated Ni(II) concentration and the total Ni calculated to be soluble (Fig. 3) above pH 6.5. Further increases in pH lead to the formation of larger insoluble polymeric species with Ni becoming less and less soluble as the pH is raised to pH 10. Although the solubility increases with pH above pH 10, the calculated solubility is still below 10^{-4} M even at pH 14. The hydrolysis diagram suggests that Ni(II) can only be loaded by a simple ion-exchange process at pH values below 6.5 where hydrolysis is

Figure 3: Calculated (9) dissolved Ni species concentrations as a function of solution pH. [Ni]Total was calculated for a 0.25M $\text{Ni}(\text{NO}_3)_2$ solution, while all other species are the predicted concentrations at infinite [Ni]Total concentrations.

negligible. Above pH 6.5, polymeric nickel clusters will be present which can either condense with surface sites on the titanate support via reactions such as:

or can condense with each other to form larger colloidal particles of nickel hydroxide. The relative amounts of nickel which are adsorbed as small clusters and as colloidal particles should be influenced by the relative availability of reactive sites on the support vs. the other clusters present in solution. In any case, the hydrolysis diagram predicts that above pH 6.5, Ni(II) adsorption should occur via hydrolysis and condensation rather than by ion exchange.

III. Nickel Loading Experiments

Combining the information obtained in our studies of the ion-exchange properties of sodium titanate with what is known concerning the hydrolysis characteristics of Ni(II), we would predict that below pH 4, Ni(II) is not adsorbed by sodium titanate, between pH 4 and pH 6.5, Ni(II) is adsorbed as a monomeric cation via an ion-exchange process, and that above pH 6.5, Ni(II) should be adsorbed as polymeric clusters and colloids via hydrolysis and condensation mechanisms. To check the above hypothesis, we have titrated acidic nickel nitrate solutions with sodium hydroxide in the absence and in the presence of sodium titanate and analyzed solution aliquots for Ni(II) as a function of pH (Fig. 4). The results obtained for nickel nitrate alone show that the hydrolysis of nickel leading to the formation of insoluble nickel hydroxide occurs between pH 7.5 and 8 (slightly higher than the pH of 6.5 predicted from simple hydrolysis diagrams, Ref. 9). Results obtained in the presence of sodium titanate suggest that as predicted, little Ni(II) is adsorbed by the sodium titanate below pH 4. Between pH 4 and pH 7.5, Ni(II) is removed from solution via ion exchange, with more Ni(II) being adsorbed

Figure 4: Plot of the amount of Ni in a 0.25M $\text{Ni}(\text{NO}_3)_2$ solution as a function of pH both in the presence and absence of a $\text{Na}_{0.5}\text{Ti}$ powder.

as the solution pH increases. Above pH 7.5, the precipitous drop in the dissolved Ni(II) concentration indicates that Ni(II) hydrolysis occurs at about the same pH in the presence of sodium titanate as in its absence. In this basic pH regime, Ni(II) adsorption should no longer occur via an ion-exchange reaction.

IV. Nickel-Loaded Catalysts

The goal of the current study was to investigate how the degree of nickel dispersion depends on the loading conditions. In particular, we were most concerned with determining the degree of dispersion when the metal was loaded solely by ion exchange since results from earlier catalytic studies^{1,4} suggest that we have good metal dispersion even at high metal loadings (> 5%) on the sodium titanates relative to materials prepared by traditional methods. Our objective was to synthesize nickel-loaded sodium titanates with equivalent nickel loadings in which the degree of dispersion would vary from individual ions to small polymeric clusters to large colloidal clusters of nickel

hydroxide. Three nickel-loaded sodium titanate catalysts were prepared (see Experimental). Sample #1 was loaded by contacting the sodium titanate powder with three aqueous solutions, each containing enough Ni(II) (from $\text{Ni}(\text{NO}_3)_2$) to completely ion-exchange for Na, at a solution pH of 5-6. Sample #2 was loaded by slowly titrating a sodium titanate slurry (initial pH near 11) with a nickel nitrate solution until 0.5 equivalents of nickel were added per equivalent of Na(I) on the support. Concurrent with the addition of the $\text{Ni}(\text{NO}_3)_2$ solution, we added NaOH to maintain the pH at 10-11. Under these conditions, nickel should be hydrolyzed within the slurry, promoting the adsorption of nickel as polymeric clusters. Sample #3 was loaded by prehydrolyzing a nickel nitrate solution to form a colloidal suspension of nickel hydroxide and then adding the sodium titanate.

The nickel-loaded titanate catalysts have been characterized using solution analyses on redissolved material and transmission electron microscopy. To date, only Samples #1 and #3 have been completely characterized. Solution analyses for Sample #1 indicate that it contains 11.1 wt% Ni and 0.5 wt% Na. This composition is close to that calculated for material which has undergone complete ion exchange (11.1 wt% Ni + 0.0 wt% Na, down from 9.3 wt% Na in the starting sodium titanate powder). There is no evidence in TEM images of this sample, taken either before or after reduction in H_2 at 400°C , for the presence of any metallic particles (Fig. 5). However, energy dispersive X-ray analysis (EDAX) of the support from the same area where no metallic particles were observed in TEM identifies only Ni and Ti rather than the Na and Ti present in the support prior to nickel loading. Therefore, all analyses of the particles confirm that complete loading of nickel has occurred via Ni:Na ion exchange. The absence of distinguishable Ni particles in the TEM images suggests that the Ni has maintained a high degree of dispersion even after 400°C H_2 reduction.

The solution analyses for Sample #3 show that this sample has almost the same nickel content (10.2 wt%) as the ion-exchanged Sample #1 (11.1 wt%). However, the analysis suggests that none of the nickel in Sample

NO NICKEL CLUSTERS ARE SEEN IN
ION EXCHANGED NI-TITANATE

Figure 5: TEM image of Sample #1 after H_2 reduction at 400 °C.

DARK-FIELD TEM IMAGE OF NI-RICH
AGGLOMERATE ON SODIUM TITANATE

— 50 nm

Figure 6: Dark-field TEM micrograph of Sample #1 as prepared.

#3 has been incorporated via ion exchange, since the sample has retained all of its sodium (10 wt%). Dark-field TEM images of the sample before reduction (Fig. 6) confirm that Ni-rich colloidal particles are observed adhering to the sodium titanate particles. TEM micrographs of the reduced Sample #3 catalyst¹⁰ clearly show the presence of large (100-500 Å) Ni particles. EDAX analyses of the bright regions in Fig. 6 contain only Ni, while the underlying particle contains Na and Ti in the same ratios found in the starting sodium titanate. Thus, no ion exchange has taken place, and all of the nickel in the samples is present as metallic Ni particles that are derived from colloidal nickel hydroxide as predicted on the basis of our nickel-loading experiments described above.

Although we expected little or no ion exchange of Ni for Na to take place in Sample #2, solution analysis showed that roughly 25-30% of the Na content was removed during preparation. This may indicate that some Ni(II) cations can undergo ion exchange for Na since Ni is present at very low concentrations during preparation (the $\text{Ni}(\text{NO}_3)_2$ solution is added slowly to the pH 11 solution containing the titanate powder). In fact, it is the low concentration of Ni that may allow control of the cluster size of nickel hydroxide when loading in this manner. Further characterizations (e.g., TEM, catalytic activity) are being performed on Sample #2 at this time.

V. BET and H₂ Chemisorption Measurements

In Table 1 we list the BET surface areas and H₂ chemisorption uptakes for the Sample #1 and #3 catalysts described above. Also listed in the table are the calculated dispersions (or the % of Ni on the surface relative to the total Ni in the catalyst) assuming 1 H/1 Ni atom. Although the ion-exchanged catalyst (Sample #1) has greater exposed Ni atoms than Sample #3, the dispersion is still considerably below expectations for Sample #1 assuming all the Ni was initially atomically dispersed on the support. However, this discrepancy can be rationalized on the basis of the BET surface area measurements made before and after H₂ reduction on Sample #1 (Table 1). The surface area

TABLE 1

	BET Surface Area (m ² /gm)	H ₂ Uptake (μmoles/gm)	%Ni Dispersion
<u>Sample #1</u>			
Before 400 °C H ₂ Reduction	275	---	---
After	86	37	1.96
<u>Sample #3</u>			
After H ₂ Reduction	---	5	0.29

of Sample #1 decreased from about 275 to 86 m²/gm after H₂ reduction at 400 °C. This dramatic reduction in surface area is accompanied by the crystallization of the titanate support which is evident in TEM, X-ray diffraction (XRD) and differential thermal analysis (DTA) measurements.¹⁰ During this structural change, a considerable fraction of the nickel could become encapsulated within densified titanate particles and, thus, the accessibility of the adsorbed Ni for H₂ chemisorption (and for reactants in a catalytic reaction) can be lost. However, the metal still accessible might remain highly dispersed. Evidence for this was described above in that metallic Ni particles were absent in the TEM images while Ni could be detected by EDAX from the same area of the sample. Further support for this conclusion was obtained from XRD measurements¹⁰ and in the catalytic activity measurements described below.

VI. Catalytic Activity of Nickel-Loaded Titanates

A good test of the dispersion of the active metal is the activity and selectivity for the hydrogenolysis of n-butane. For example, it is well known¹¹ that the hydrogenolysis of saturated hydrocarbons, or the

rupture of carbon-carbon bonds by hydrogen, are structure sensitive; that is, their rates per surface metal atom (specific rates) vary with the percentage of metal exposed on the catalyst (i.e., the dispersion). Typically, the specific rates are found to decrease with decreasing dispersion (increasing metal particle size). It has also been reported that highly dispersed Ir catalysts are particularly selective for ethane by preferential scission of the central C-C bond in n-butane.¹²

In Fig. 7, we plot the specific rate for n-butane hydrogenolysis over Sample #1 and Sample #3. Dramatic differences in both the rate and activation energy were observed. The catalyst prepared by ion exchange of monomeric Ni^{+2} cations (Sample #1) is up to two orders of magnitude more active than the precipitated Ni catalysts. These results will be discussed in more detail in a forthcoming publication.¹⁰ For the purposes of this report, at least part of this difference in activity can be ascribed to a particle size effect; notably, that the higher activity obtained on the ion-exchanged Ni catalyst is due to its higher dispersion which correspondingly gives rise to a smaller amount of less active, close-packed Ni surfaces in the catalyst.¹³

Fig. 8 displays the results obtained for the selectivity for C_1 , C_2 and C_3 paraffin hydrocarbons as a function of temperature on Sample #1 (ion-exchanged) and Sample #3 Ni catalysts. It can be seen that the catalyst prepared by ion exchange is very selective for C_2 hydrocarbons (ethane) at temperatures below 540 K. At higher temperatures (> 550 K), methane is the predominant product. In the case of the catalyst prepared by pre-hydrolysis (Sample #3), methane is the primary product for all temperatures studied. These results confirm our earlier conclusions concerning the dispersion of nickel in the two catalysts based on the TEM and chemisorption data. That is, reactivity on Sample #3 is characteristic of large metal particles while the selectivity observed on Sample #1 clearly indicates that at most very small, highly dispersed Ni particles are formed even at these high metal loadings (10%).

Figure 7: Arrhenius plot of the rate of n-butane hydrogenolysis over Sample #1 (ion-exchanged Ni catalyst) and Sample #3 (precipitated Ni catalyst).

Figure 8: Selectivity for C₁ (CH₄), C₂ (C₂H₆), and C₃ (C₃H₈) hydrocarbon formation from the hydrogenolysis of n-butane over Sample #1 and Sample #3.

Summary and Conclusions

We have prepared and studied the properties of a sodium hydrous titanium ion-exchange material, which has shown great promise for use as a heterogeneous catalyst support. In these studies we have identified the solution conditions (e.g., pH) in which the sodium titanates contain sites for the adsorption of either metal cations or anions. For the exchange of Na for Ni(II) cations, solutions with a pH of 5 or more are required. However, Ni(II) undergoes extensive hydrolysis and condensation reactions above a pH of about 7-8 which competes with ion-exchange onto the support when both are present in solution. We have prepared three Ni-loaded hydrous titanates under different solution conditions to compare their material and catalytic properties. The catalysts were characterized by solution analyses, TEM, hydrogen chemisorption, BET surface area measurements, and the activity and selectivity of the n-butane hydrogenolysis reaction. The catalyst prepared via ion exchange displayed a high degree of selectivity for ethane from scission of the central C-C bond in n-butane indicative of highly dispersed metal even at the loading of 10% used in this study. The absence of metallic Ni in TEM images of this catalyst is further support for such a morphology. This is good evidence that atomic level dispersions of Ni are present in the as prepared catalyst and that high metal dispersions are maintained upon hydrogen reduction at 400 °C. However, H₂ chemisorption indicates that only a small portion of the Ni is accessible on the surface of the catalyst. We believe that the crystallization of the titanate support that accompanies the reduction of Ni at 400 °C in H₂, encapsulates most of the metal within the densified titanate particles making it inaccessible to gas-phase species.

The high dispersion of the metal in catalysts prepared by ion exchange onto the hydrous titanate supports may well explain the high activity (on a per gram of metal basis) of these catalysts relative to catalysts prepared by more conventional methods.^{1,4} In these latter studies, the metal is reduced in-situ during reaction at much lower

temperatures than used here to reduce Ni. Thus, the accessibility of the metal may not be compromised by the restructuring of the catalyst support material. In the future, we will investigate more moderate metal reduction methods, more easily reducible metals, and modifications of the synthesis of the sodium titanate powders. In this way, we hope to maintain the accessibility of the metal while still achieving the good dispersion at high metal loadings afforded by the use of ion exchange to prepare a catalyst on the hydrous titanates.

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VPI-1 - INVESTIGATION OF PROPERTIES AND PERFORMANCE
OF CERAMIC COMPOSITE COMPONENTS

K.L. Reifsnider, W.W. Stinchcomb, T.J. Dunyak

Materials Response Group
Engineering Science and Mechanics Department
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061
(703) 961-5316

INTRODUCTION

The art and science with ceramic composites has reached the critical threshold of large scale applications to primary engineering structures. Hence, many applications associated with heat exchangers, regenerators, turbines, and heat engines (to name a few) are being planned. The primary constraint on making this major step to applications is the extent to which the associated technical community can make the transition from properties of materials to the performance of engineering components.

Making this transition requires comprehensive characterization and understanding (i.e., philosophy and rigorous modeling) of long-term behavior. For example, information from quasi-static tests, modulus of rupture tests and fracture toughness tests are not sufficient to design a composite component such as a heat exchanger tube which may experience multiaxial stresses and anisotropic fibrous reinforcement. The present research effort is directed towards meeting these needs for the transition from properties to performance. In general, the program is a pioneering effort to make a first step beyond the limited characterization of small samples and coupons to the comprehensive mechanical characterization of composite engineering components such as tubes subjected to static and cyclic multiaxial loading and elevated temperature over various time periods.

Objectives - Purpose of the Research

The central objective of the present program is to develop an understanding of the mechanical behavior of advanced composites subjected to elevated temperature and dynamic (cyclic) loading, to develop a test system and test methods that will be used to obtain the properties and performance information required to design engineering components made from ceramic composite materials, and to provide critical and comprehensive evaluations of such materials to material synthesizers and developers to support and enhance progress in ceramic composite material development. Specific objectives include the following.

1. To design and construct a mechanical test device, using a servohydraulic test frame designed for multiaxial loading.
2. To establish the room temperature response of several material types of ceramic composite tubes to quasi-static uniaxial loading, especially the strength, stiffness, and failure modes of those tubes, the statistical variations of those characteristics, and the mechanistic relationship of the microstructure and damage state associated with each material system to the observed response.
3. To establish the response (as described in 2) to cyclic loading.
4. To establish the response (as described in 2 and 3) at elevated temperature up to 2500°F.
5. To develop mechanistic models which are capable of predicting the strength (or residual strength) of ceramic composite tubes subjected to various load histories and temperatures as described above, using the disciplines of mechanics, physics, and the understanding of behavior obtained from experimental investigations.

6. Establish the nature of the need for subsequent work dealing with additional parameters such as other generic component shapes, other atmospheres, other material systems, other loadings or load histories, or other response characteristics (dynamic, magnetic, etc.).

Approach

The thirty month program is divided into four different tasks. These tasks are outlined in Table 1.

Task 1:

The program begins with a major thrust of planning, literature review, design and basic setup. A major part of the Task 1 effort has been directed towards the purchase and installation of a multiaxial test frame as a starting point for the construction of the high temperature test system. The quasi-static test series will be planned based on a review of data from previous work. The basic design of the test chamber, grips and specimen will be generated and construction initiated. The specimen design will be a cooperative venture with the specimen supplier (United Technology Research Center), the Materials Response Group, and the test chamber design group (Instron Corporation).

Two major requirements of the program will be the acquisition of data on the internal state of damage of the material and modeling the damage development in the material. Therefore, Task 1 will involve a literature review and planning for nondestructive test methods, and a literature review of damage models for cyclic loading of brittle matrix composites.

Task 2:

The axial-torsional load frame will be used to conduct uniaxial, quasi-static room temperature tensile tests on ceramic composite specimens. These tests will be used to establish baseline data for the material systems under quasi-static loading, to identify failure

Mechanical Characterization of High Temperature Composites
Program Tasks for Phase I (2.5 years)

Table 1

Schedule (yr.)	1 (12 mos.)		2 (12 mos.)	3 (6 mos.)	Phase II...
Task	1	2	3	4	
Construction of Test Device	Purchase of Test Frame -- Design of Test Chamber and Grips	Construction of Room Temp. Device, Design of High Temp. Equipment	Construction of High Temperature Device	Testing and Refinement	
Quasi-static Room Temperature Characterization		Uniaxial Tension Tests	Tension-Compression Tests, Damage Analysis	Damage Analysis	
Cyclic Room Temperature Characterization			Uniaxial Tension, Damage Analysis	Tension-Compression Damage Analysis	
High Temperature Characterization			Preliminary Tests, Quasi-static	Uniaxial, Cyclic, Damage Analysis, Multiaxial Cyc*	
Modeling	Literature Review	Identification of Failure Modes	Nondestructive Identification of Damage Modes	Formulation -- Predictions	
Planning of Investigations	Quasi-static Series	Cyclic Series	High Temperature Series	Verification Series Future Work **	

* Demonstration multiaxial tests will be conducted during task 4.

** Future work will include multiaxial, high temperature tests if the program is continued into Phase II.

Properties and Performance of Ceramic Composite Components

modes for subsequent modeling, and to make refinements in the mechanical test system and specimen geometry if necessary. Concurrently, the high temperature equipment for the system will be designed and construction initiated. In addition, development of nondestructive test methods will be initiated during the test program to follow the damage development in the specimen. The final Task 2 activity will include planning for the room temperature cyclic test series.

Task 3:

The final step in the high temperature test system construction will be conducted in Task 3. During the construction period, tension-compression quasi-static testing at room temperature and high temperature will be conducted to initiate the study and modeling of the failure of ceramic composite specimens and the damage processes that lead to failure under sustained cyclic loading. Final material system choices will also be made, and the development of nondestructive test methods will continue. The final activity in the Task will be the planning of a high temperature test series, to include high temperature tension-compression loading.

Task 4:

Primary objectives of Task 4 are to conduct a rigorous program of high temperature testing to refine the test specimen, and to begin to formulate a model of strength that can be used at high temperature and for residual strength prediction after damage has occurred. This will be a fully operational shakedown phase with all systems in operation. The focus of the program will shift from construction of the test system to characterization of the material system selected in Task 3. Special attention will be given to the interpretation of the results and the development of a mechanistic damage model. The final activity in Task 4 will be the planning of a test series for the purpose of verifying the validity of the model and associated concepts.

Discussion of Previous Work

Over the initial six months of the program several significant milestones were completed. A major milestone involved writing specifications for and ordering the biaxial test frame. The high stiffness test frame is rated at 100 kip axial load and 50 kip-in torsional load. The actuators and load cell are rated at 50 kip axial and 25 in-kip torsion. A picture of the test frame and control console is shown in Figure 1. The preliminary release of the test specimen design represented another major milestone. The specimen has a tubular geometry with cylindrical ends for gripping (see Figure 2). The specimen design was supported by a detailed finite element analysis. The other milestone in the first six months involved the selection of a preliminary material system. Based on the current manufacturing capabilities, an HMU Graphite/Borosilicate glass specimen supplied by the United Technologies Corporation was selected for the initial series of tests. It is possible (indeed, likely) that the rapid development of ceramic composite materials will dictate a material system of primary interest which is not apparent now. Therefore, the material system for the test specimens can and probably will be changed later in the program.

DISCUSSION OF CURRENT ACTIVITIES

The remainder of the Task 1 activities were completed in the past six months. These activities included

- Reviewing the literature in the areas of nondestructive evaluation of ceramic composite materials and modeling of damage in such materials.
- Resolving the concerns of the specimen suppliers and the grip manufacturers over the specimen design and initiated fabrication of test specimens.

Figure 1. Instron high stiffness axial-torsional testing machine and control console.

Figure 2. Cylindrical ceramic tube specimen.

- Planning the quasi-static test series.

In addition, several activities in Tasks 2 and 3 were initiated or completed. These activities are summarized below.

- Constructed and accepted the biaxial test frame.
- Initiated investigation of nondestructive test methods to monitor damage development.
- Initiated the development of a critical element model which will be used to predict life or residual strength of a ceramic composite specimen.

All of these areas will be discussed in detail in the following sections.

Literature Review

A literature review was conducted during this report period. Several areas were surveyed including high temperature test methods and equipment, nondestructive evaluation methods, damage modeling, and brittle matrix composite test results. In most cases the papers covered testing of small coupons in bending. In addition, only two papers considered the fatigue behavior of these materials^{1,2}. Although the bulk of the literature review has been completed, the literature search will continue throughout the program as new work is published.

Of all the papers reviewed, a paper by Marshall and Evans³ proved the most interesting. A portion of the paper considers the effect of surface damage on matrix cracking. Controlled surface flaws were introduced into the specimens by Vickers and Knoop indentations. Some of these flaws produced cracks and chipping which extended across more than 10 fibers. In all of the tests, the stress level of the matrix cracks was not altered by the presence of the induced flaws, and in

most cases, the first matrix cracks did not even initiate from the indentation. Based on these results, it appears the performance of brittle ceramic matrix composites may be governed by factors similar to those in fiber reinforced epoxies as contrasted with standard ceramics which may have the performance governed by a single microscopic flaw.

Specimen Fabrication

The specimen design was finalized and 8 specimens have been ordered. These specimens are currently in fabrication and delivery is expected in late November. In order to accommodate the grip design tolerances, the outside diameter of the grip regions will be machined to $\pm .0005$ inches after molding. There is some concern about introducing microcracking and residual stress fields as a result of the machining operation. These concerns will be resolved during the preliminary uniaxial and room temperature cyclic tests. In addition to the graphite/glass specimens, 25 borosilicate glass specimens were ordered. These glass specimens will be used for system check out purposes prior to loading the reinforced specimens.

Planning the Quasi-static Tensile Tests

A couple quasi-static tension tests have been planned at room temperature. The actual number of tests will depend on the reproducibility of the results and the need to resolve of any unexpected problems. The tests will be run from a preloaded state to complete separation in load control with constant monitoring of load, stroke and strain. Prior to the test, the specimen will be C-scanned to locate any large defects or density variations. After the tests, C-scans will be repeated, and fractography analyses will be conducted at the failure surfaces. In addition, acoustic emissions may be monitored throughout the tests.

Acceptance Tests

Construction and check-out of the Instron servo-hydraulic multiaxial testing machine have been completed. The design of the two column test frame gives an axial stiffness of 5.0×10^6 lbs/in and a torsional stiffness of 3.8×10^6 in-lbs/deg at a crosshead to base separation of 40 inches. Check out tests were conducted at the Instron plant in Canton, MA.

The first check-out test was demonstration of axial, torsional, and biaxial performance using a cylindrical steel bar specimen. The machine operated satisfactorily in each operational mode over a range of cyclic command function amplitudes, waveforms, and frequencies. The required performance specifications were met.

The second check-out test consisted of a series of monotonic, cyclic load, and creep tests on button-head, silicon nitride specimens having a reduced diameter, cylindrical test section with a cross sectional area of 0.044 sq. in. All tests were conducted at room temperature. Strains were measured using a 0.5 inch gage length extensometer. Load to failure tests were conducted in stroke control mode. Cyclic load and creep tests were conducted in the load control mode. The loading history consisted of the following components:

1. Monotonic tensile loading of a buttonhead, silicon nitride specimen in stroke control; stroke rate: 0.2/in/min; load to fracture; record load and strain throughout test.
2. Using a second specimen, apply four cycles of a triangular waveform in load control at 0.1 Hz; load range: 50 to 1000 lbs (2 to 38% of expected fracture load); record load - strain response for each cycle.
3. Apply approximately 1000 cycles of 50 to 1000 lb cyclic loading at 1 Hz; record load and strain waveforms.
4. Record load - strain response after cyclic loading.

5. Ramp load to 1000 lbs and hold for one hour; record load and strain signals.
6. Reduce load from 1000 to 100 lbs; reload to 1400 lbs; unload to 100 lbs; record load -strain response.
7. Switch control mode to STOKE and reload to fracture at a rate of 0.02 in/min; record load - strain response; record load at fracture.

All tests were performed successfully. An initial tensile strength of 59.7 ksi and a strain at failure of 0.015% were measured for the first specimen. After the cyclic and creep loads had been applied to the second specimen, it failed with a residual tensile strength of 58.5 ksi and a strain of 0.014%. Youngs modulus, calculated as the slope of the linear portion of the stress-strain curves, did not change during the loading history.

Investigation of Nondestructive Test Methods

Two nondestructive methods were investigated to assess the damage in the specimens. C-scans on a plate sample of the graphite/glass material were conducted. Results indicate the method may be used to assess variations in density and locate some large defects. The C-scan apparatus is now being modified to handle tubular specimens.

The second nondestructive test method under investigation involves the use of acousto-ultrasonics (AU). The AU method is a relatively new nondestructive technique which consists of the introduction of stress waves at one point in the material and the detection of these waves at another point. A pulse generator/reciever is used to produce an electrical pulse which is introduced into the material as a stress wave through an ultrasonic transducer. The pulse is detected by another ultrasonic transducer. The received signal is then amplified and digitized. Analysis of the signal is then performed by a PC to produce a quantitative measure of the internal state of the material.

The AU method is still relatively undeveloped for brittle matrix materials. However, progress is being made. Unfortunately, neither of these methods can be used in situ. Therefore, alternative methods of monitoring damage need to be investigated.

The Critical Element Model for Life Predictions

The critical element concept will be used for modeling the remaining strength and life of the ceramic materials to be tested. The approach is based on a thorough and precise determination of the nature of the failure mode associated with the strength or life reduction to be calculated and of the attendant damage development process. The model is created for each such failure mode. The controlling reduction mechanism is determined by running the model for all such modes thought to be operable in a given situation and comparing the predicted remaining strength and life.

Based on this experimental information, a "critical element" is identified as the material element or volume whose failure defines the failure event for the global laminate, component or material volume. For fiber dominated laminates, for example, the critical element may be the fibers in the ply which has an orientation most nearly aligned with the principle load direction. For compression failure, the critical element may be the undelaminated ligament which finally buckles or crushes, ect. The model consists of a continuous evaluation of the state of stress and state of material in the critical element for a given failure mode due to cyclic loading, variations in temperature, or other influences which are applied over the term of expected life of the component in question.

The state of material is represented by updated properties (such as strength and stiffness), i.e., by continuum constitutive relations and qualities. The state of stress is determined by solving the appropriate boundary value problem for the critical element concerned, using macro- or micro-mechanics. The state of stress in the critical element is a function of loading history since the development of damage continuously changes the local geometry and the manner in which

the load is distributed among the material elements at the local level.

Changes in the stress state at the local level are a result of the changes in the stiffness of the material that undergoes matrix cracking. These changes are determined from experimental measurement when such data are available. However, these changes can also be estimated by "discounting" the stiffness of the material that fails according to an appropriate failure theory such as the Tsai-Hill criterion, and examining the global stiffness change associated with the known applied load level. As sub-critical elements of material fail (by matrix cracking, ect.), the stress that was borne by those elements is transferred to the remaining unbroken material, the critical elements. This transfer increases the rate at which the critical elements degrade and accelerates the reduction of strength.

The strength of the critical element may also be degraded. Elevated temperature or aggressive environments such as chemicals, atomic oxygen, ect. may cause static failure to occur in the critical elements. This change must be measured independently in the laboratory and a phenomenological representation of the reduction established. The model to be constructed in the present investigation will have the capability to include such relationships. This capability will include the prediction of creep rupture lives, for example.

Once the state of stress and state of strength has been set for a given point in the loading history, as described above, the remaining strength is calculated. Strength reduction is actually calculated by the relationship illustrated in equation [1].

$$S_r = 1 - \int_0^t (1 - F_a) i (n/N)^{(i-1)} d(n/N) \quad [1]$$

where S_r is the remaining strength, F_a is the current value of the failure function in the critical element, n is the current number of cycles, N is the life of the critical element in the current stress state, and i is a constant equal to 1.2. The value of the failure

function changes as a function of the number of cycles due to the changes in stiffness at the global and local level, and the changes in the material strengths. The model calculates the remaining strength by numerical integration of the integral shown in equation [1]. Since the remaining strength is calculated from an integral, variations in the applied load as a function of time (spectrum loading) are easily handled.

Fundamental elements of the model are in place. Current efforts are directed to the generation of the representations necessary to represent the high temperature degradation of the materials to be modeled. Also, the first task in the laboratory will be to identify the critical element associated with the failure of the materials in this program under cyclic loading at room temperature and elevated temperature. That information will be used to establish the correct representation of the local stress state in the critical elements when damage develops, so that the evolution equation, equation [1], can be evaluated.

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PART III - ALLOY DEVELOPMENT AND MECHANICAL PROPERTIES

B&W-2 - EVALUATION OF THE FABRICABILITY
OF ADVANCED AUSTENITIC TUBING

S. E. LeBeau

Babcock & Wilcox Research
Alliance, Ohio 44601

INTRODUCTION

The U.S. Department of Energy Advanced Research and Technology Development (AR&TD) Fossil Energy Materials Program has undertaken a six-year activity to investigate candidate alloys for advanced steam cycle superheaters and reheaters. One task in this program addresses the problem of fabricating tubing from alloys containing controlled amounts of minor element additions and cladding or surface treating the tubing for optimum corrosion resistance. The specific alloys have been defined through an alloy screening program that is concerned with strength and metallurgical stability at temperatures in the range of 650 to 760°C.⁽¹⁾ Although some indication of the fabricability of candidate alloys was derived in the course of producing 13-mm thick plate for screening tests,^(2,3) the fabricability, weldability, and surface-treating capability of the alloys can best be assessed by the production of commercial-scale tubing.

The scope of the current program consists of melting experimental alloys, conditioning of ingots and forging of ingots into extrusion billets, and production of seamless tubing. A portion of some of the sample tubing will be clad on the outside with high-chromium, high-nickel alloys (Alloy 671, 690) for corrosion protection. Specific details on each of the processing routines and results of chemical and metallurgical testing of tubing produced to date are presented in a recent report issued to Martin Marietta Energy Systems⁽⁴⁾. Samples of the tubing produced under this task will be used in complementary tasks to examine the mechanical behavior, weldability, and fireside and steamside corrosion of the tubing.

DISCUSSION OF CURRENT ACTIVITIES

The current contract calls for the production of seamless tubing via commercial methods of two development alloys: a modified type 316 stainless steel and a modified 800H alloy. The tubing is to be produced from both alloys via conventional production methods as outlined in Figure 1. In addition to base alloy tubing, representative samples will be clad on their outer surface and coextruded into a metallurgically bonded bimetallic tube to provide enhanced fireside corrosion resistance for these alloys. Production of tubing on a commercial basis will assess the fabricability of these developmental alloys as well as provide test material for complementary tasks involving mechanical behavior, weldability and fireside and steamside corrosion testing.

***Process Routines for
Austenitic Alloy Tubing***

Figure 1. Manufacturing Process Routines for Seamless Austenitic Alloy Tubing.

To date, seamless tubing has been successfully produced from one of the "lean" stainless steels (14Cr-16Ni) investigated in earlier studies at ORNL. The alloy extrusion billet stock was produced by vacuum induction melting, electroslag remelting and was cast into a 33 cm. diameter ingot. The cast ingot was hot forged to an extrusion billet diameter of 14.6 cm and the surface rough bar peeled prior to extrusion. Two billets were hot extruded into seamless tubing directly without any further processing. Two additional billets of the same "lean" stainless alloy were clad with an Inconel 671 alloy via powder metallurgy techniques (see Figure 2).

Figure 2. Schematic Diagram Comparing Powder Metallurgy vs. Conventional Methods of Producing Clad Extrusion Billet.

The clad billets and unclad billets were both extruded into seamless tubing (6.35cm OD x 12mm wall) using standard commercial equipment used to manufacture stainless seamless tubing. Based on the response of the extrusion tooling and equipment during the production run, it appears that the lean stainless alloy in either a straight or clad condition extrudes on a relatively easy basis comparable to conventional stainless alloys.

The extruded tubes were subjected to chemical analysis and ultrasonic testing and select metallographic sections were examined prior to shipment to ORNL for further testing. Figure 3 displays macrophotographs of a transverse section of the OD clad tubing produced. The integrity of the bond between the cladding alloy and base metal is demonstrated by the response of the tube section to a hydraulic flattening test. The tubing samples produced were within the the specified dimensions and chemistry ranges requested by ORNL. Ultrasonic testing as well as metallographic sections confirmed the integrity of the bond on the clad tubing samples evaluated.

No unusual difficulties relative to conventional stainless steels were encountered during melting, hot forging or extrusion of the experimental alloys. Future studies will be expanded to include the modified 800H base alloy, evaluate alternative cladding alloy compositions and cladding methods. The response of the base alloys to cold working (pilgering) operations will also be included in future efforts.

Figure 3. Macrophotographs of Coextruded Bimetallic Tubing (14Cr-16Ni Steel with 671 Alloy Cladding) in As-Extruded Condition and After Hydraulic Flattening Test.

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CSM-2 - INVESTIGATION OF THE WELDABILITY OF
DUCTILE ALUMINIDES

M.C. Maguire*, G.R. Edwards*, and S.A. David†

Center for Welding and Joining Research
Department of Metallurgy and Materials Engineering
Colorado School of Mines
Golden, Colorado 80401

†Metals and Ceramics Division
Materials Joining Group
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6095

INTRODUCTION

Ni₃Al and alloys based on this long range ordered intermetallic compound represent a possible new class of high temperature material. The most promising feature of Ni₃Al is its increasing yield stress with temperature, up to about 700°C. However, polycrystals are subject to brittle intergranular fracture at temperatures above 500°C, despite the presence of boron microalloying additions. In addition, welds made on this material show a tendency for intergranular heat-affected zone (HAZ) cracking. Previous investigators have shown that this cracking behavior can be linked to alloy composition^{1,2,3}, environmental effects^{4,5} and, more recently, substructural morphology⁶. This joint Colorado School of Mines and Oak Ridge National Laboratory investigation was established to develop a fundamental understanding of the cracking phenomenon in this material, and to exploit this knowledge to develop methods for reducing cracking tendency. The current investigation is aimed at substructural refinement by antiphase domain structures (APD), which, as will be described, have been shown to be an effective means to increase hot ductility.

DISCUSSION OF CURRENT ACTIVITIES

The focus of investigation is currently centered on two features of the domain microstructures described previously⁷: (1) the effect of domain microstructure on hot ductility and weldability, and, (2) domain structure

thermal stability. The current alloy of interest, designated IC-50-8, contains nominally in atomic percent: 18Al - 8Cr - 0.5Hf - 0.10B. Earlier studies of alloys with varying chromium levels indicated that large fractions of the microstructure can be disordered at high temperature when chromium levels approach 8 percent. Since disordering prior to melting is a prerequisite for domain formation, IC-50-8 was selected for continued work to characterize domain microstructures.

Chromium decreases the ordering temperature of Ni_3Al bringing about significant disordering prior to melting. In an earlier study, disordering was accomplished by annealing at 1250°C for 900s, followed by oil quenching to produce a microstructure containing fine APD's⁷. However, since the ordering reaction is a first order phase transformation, indicating that disordered and ordered phases can exist within a microstructure, ordered γ' islands are still present at 1250°C . At this temperature, these islands are surrounded by disordered γ . Upon quenching, the disordered γ matrix rapidly reorders by the formation of a fine domain structure, leaving the ordered islands relatively unchanged. In the current work, the annealing temperature was raised to 1290°C to reduce the amount of γ' present prior to quenching.

Alloy preparation and hot ductility test procedures, have been described elsewhere⁸. Samples of 6mm thick IC-50-8 sheet were annealed for 900s at 1280°C and oil quenched. The resulting microstructure contained 80 percent of the domain containing constituent. That is, about 80 percent of the microstructure disordered at 1280°C , subsequently reordering to form domains during the quench. Oil quenching from a 900s anneal at 1250°C generated domains in 72 percent of the microstructure.

Hot ductility test results for the material quenched from 1280°C are shown in Fig. 1. Also included are hot ductility data for the same alloy quenched from 1250°C , and furnace cooled from 1190°C . Both quenched microstructures exhibit better ductility than the furnace cooled material in the test temperature range from 20 to 700°C . There is also a slight increase in ductility above 1000°C in material quenched from 1280°C . Furnace cooling allows the domains to coarsen significantly, ultimately reaching the size of a single grain. Hence, an oil quenched microstructure has better hot ductility than one which was slowly cooled. In addition, the higher annealing temperature result in a more extensive

Figure 1. Variation of hot ductility, measured as reduction in area, as a function of test temperature for alloy IC-50-8 after three different heat treatments.

domain structure formation.

Yield and peak flow stress data for IC-50-8 quenched from 1280°C are shown in Fig. 2. Previously reported data for the same alloy quenched from 1250°C⁸ showed that flow stress below 600°C was not significantly altered by an increase in annealing temperature. However, at 1000°C the peak stress increased from about 200 MPa to above 350 MPa as the annealing temperature changed from 1250°C to 1280°C. Figure 2 also shows that the yield stress peaks near 750°C, and the increase in yield strength over the room temperature value is only about 100 MPa.

Samples for transmission electron microscope (TEM) examination were cut from as-quenched, unstrained IC-50-8. Thin foils were prepared by standard wafering, grinding, and electropolishing techniques described by other investigators¹. Prior to final thinning, the disc was bent slightly to generate a small amount of plastic deformation. The disc was subsequently thinned and examined in a Phillips EM400 operating at 120kV. Figure 3 shows the TEM micrographs for two regions. Figure 3(a) shows a region which contains domain structure. The larger material in the center

Figure 2. Yield and peak flow stress for alloy IC-50-8 quenched from 1280°C, as measured during the hot ductility test.

is an ordered island* surrounded by smaller ordered domains. Figure 3(b) illustrates dislocation configurations in a large ordered island, typical of a microstructure with no domains, such as slowly cooled material. Figure 3(a) indicates that the length of a superlattice dislocation becomes much shorter in the fine domain microstructure. This leads to the observation that deformation processes are strongly affected by the presence of domains. Namely, slip will be dispersed throughout the microstructure. If a material is subject to grain boundary fracture, then by dispersing the slip one reduces grain boundary loading, and improves ductility. This sort of behavior is suggested to be responsible for the results observed here.

A study of the thermal stability of the domains was also undertaken. If quenched-in domains are to be effective in reducing the tendency for HAZ cracking and intergranular fracture at high temperatures, then they must be stable for a given thermal cycle. Standard isothermal annealing

*The difference between an ordered island and a domain was alluded to previously, but, for the purposes of this investigation, the difference arises in their formation. Ordered islands consist of material which remained ordered at the annealing temperature. Domains formed from disordered γ which reordered upon cooling.

Figure 3. Bright field TEM micrographs of IC-50-8 slightly strained at room temperature showing the variation in dislocation structure in the (a) fine domain substructure, and (b) large ordered island.

treatments at 500, 700, and 900°C were conducted to determine domain coarsening kinetics. Domain sizes were measured by TEM using linear intercept techniques with no geometrical correction factor.

Figures 4-6 present the domain size coarsening behavior for the each annealing temperature. Coarsening appears to be very slow at 500 and 700°C, but begins to hasten at 900°C. If standard D^2 kinetics apply, then a typical $D^2 - D_0^2$ plot should be linear; however, when the data for the 900°C anneal is plotted in that fashion, as shown in Fig. 7, a linear fit is not observed. A better fit is obtained with a growth exponent of 7.6, shown in Fig. 8. Although no physical explanation exists as yet for such a high exponent, it does indicate that domain growth in this alloy is an extremely sluggish process. A typical Arrhenius plot of the data is shown in Fig. 9. If only the data for the 700°C and 900°C are considered, domain growth has an apparent activation energy of 55 kcal/mole. The data for the 500°C anneal presents some difficulty, as seen in Fig. 9. The

Figure 4. Domain size dependence on annealing time at 500°C for IC-50-8.

Figure 5. Domain size dependence on annealing time at 700°C for IC-50-8.

Figure 6. Domain size dependence on annealing time at 900°C for IC-50-8.

Figure 7. Domain coarsening behavior for alloy IC-50-8 when analyzed by standard D^2 kinetics. The data does not fit the linear behavior usually observed.

Figure 8. Log-log plot of domain coarsening behavior for IC-50-8 at 900°C. A growth exponent of 7.6 is shown to be a better empirical fit.

Figure 9. Typical Arrhenius-type plot for domain coarsening kinetics of alloy IC-50-8 annealed at 900°C. The data at 500°C is considered somewhat suspect due to difficulties in measuring small changes in domain size.

activation energy for growth in the 500°C to 700°C range appears to be much less, about 5 kcal/mole. The sensitivity of activation energy measurement is very small at lower temperatures due to the small changes in domain size, leading to some question of the apparent activation energy of 5 kcal/mole. This value is too low to be considered valid for a process such as domain growth. Additional experiments are currently concentrating on two other temperatures, 800 and 1000°C, to clarify the domain coarsening kinetics.

This recent data reinforces previous ideas about the strong effect of domains on the microstructural development and mechanical properties of ordered alloys. A domain structure has two favorable effects: (1) it increases the ductility, and (2) increases the strength - two properties which are usually pitted against each other. A stable domain structure could potentially be an effective means to improve the high temperature ductility of these promising intermetallics.

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CU-2 - MECHANICAL PROPERTIES AND MICROSTRUCTURAL STABILITY
OF ADVANCED AUSTENITIC ALLOYS

R.D. Black, B.D. Coulombe, and Che-Yu Li

Department of Materials Science and Engineering
Cornell University
Ithaca, NY 14853-1501

INTRODUCTION

The goals of this project are to (a) obtain mechanical property data which can be used to screen alloys developed for use in advanced steam cycle plants, and (b) to characterize the long-term mechanical properties of the promising alloys. The previous report¹ emphasized correlation of mechanical properties of the 17/14 CuMo reference alloy with its microstructural evolution during aging at 800°C for times up to 2146 hrs. The report concluded that during the initial 200 hrs of aging there was a 10-30% drop in flow strength as a result of coarsening of MC-type precipitates. After the initial drop the flow strength of the alloy was found to level off. This leveling off was consistent with the decreased ripening rate of the MC-type precipitates.

In this period further mechanical property data of 17/14 CuMo specimens aged up to 17,970 hrs are reported. Changes in flow strength with aging time will be considered in terms of known phase formation. The alloys screening portion of the program was also continued -- specimens of a laboratory heat modified 800H alloy, as well as specimens taken from a section of a spin-cast* tube of a modified 800H alloy, were load relaxation tested in various states of thermo-mechanical pretreatment. The results of these tests are discussed and the tube material compared with the laboratory heat material, a laboratory heat unmodified 800H alloy, and a laboratory heat modified 316 stainless steel alloy (CE3). A laboratory heat modified 316 stainless steel similar to alloy CE0, but with an increased nitrogen level, was also load relaxation tested.

* centrifugally cast and cold pilgered

DISCUSSION OF CURRENT ACTIVITIES

Experiments

Specimen Preparation

Compositions of the 17/14 CuMo alloy, a modified 800H alloy (AX3), a modified 800H alloy fabricated in tube form (X-3891), an unmodified 800H alloy, a modified 316 alloy (CE3), and a modified 316 alloy with an increased level of nitrogen (MS4-1) are given in Table I. All materials, except for the tube material, were in laboratory heat form.

The laboratory heat materials were received as mill-annealed sheets, cold rolled to approximately 0.76 mm, and then fabricated into dog-bone type tensile specimens with a nominal gauge width of 3.55 mm and a nominal gauge length of 12.7 mm. Fabrication was performed such that the gauge length was parallel to the rolling direction. In the case of the tube material, 0.76 mm radial sections were cut along the longitudinal direction of the tube. These sections were fabricated into dog-bone type tensile specimens as described above.

After fabrication specimens typically received an 1150°C solution treatment for 1 hr. After solution treating some of the specimens were cold worked to a level of 2 or 5%. All of the specimens were then aged for 2 days at 850°C or, in the case of the 17/14 CuMo specimens, their respective aging time at 800°C.

Mechanical Testing and Data Analysis

Because the details of the load relaxation testing are given elsewhere² only a brief outline of the test is given below.

The load relaxation test consists of loading a specimen in an Instron-type testing machine to a particular load or strain level. Once this level is reached the cross-head is fixed. Load relaxation occurs by conversion of the elastic strain in the test system into plastic strain in the specimen. Specimens are usually tested at four increasing level of plastic strain up to 5%. The data is presented as a $\log(\text{true stress}, \sigma) - \log(\text{inelastic strain rate}, \dot{\epsilon})$ flow curve. All of the load relaxation data presented in this report was obtained at a temperature of 700°C. Only the data obtained at the nominal yield strain and at 5% plastic strain are reported.

So as not to involve work hardening considerations, the flow curve at the yield strain is usually used as a means to compare different thermo-mechanical

pretreatments. This method provides quantitative information at low strain rates where the data is completely plastic, but only qualitative information at high strain rates where the data often exhibits a large anelastic component.³ For the purpose of analyzing and comparing the 17/14 CuMo load relaxation data the flow strength at a low strain rate (10^{-8} s^{-1}) was used as a measure of the creep properties of the material.

Table I. Alloy Chemical Compositions (wt%)

Element	17/14 CuMo	AX3	X-3891 *	800H	CE3	MS4-1
Cr	16.29	20.60	20.85	19.50	14.53	14.00
Ni	13.86	30.60	31.08	31.96	16.18	16.00
Al	-----	-----	0.02	0.43	0.03	-----
Mo	1.96	2.00	2.27	-----	1.96	-----
Cu	3.07	-----	0.03	-----	1.96	-----
P	0.01	0.03	<.01	-----	0.07	0.05
B	-----	0.01	0.01	-----	0.01	0.01
N	0.03	0.03	0.01	-----	0.01	0.04
V	0.07	0.52	0.47	-----	0.56	0.50
Ti	0.10	0.36	0.29	0.42	0.09	0.30
Mn	0.83	2.00	1.93	0.90	1.68	2.00
S	0.02	0.01	0.01	-----	0.01	-----
Si	0.95	0.22	0.24	0.24	0.21	0.40
Nb/Ta	0.45	0.24	0.20	-----	0.11	0.10
C	0.10	0.09	0.10	0.08	0.09	0.10
Fe	bal.	bal.	bal.	bal.	bal.	bal.

*pour end

Results

Alloy 800H

Figure 1 compares load relaxation data of the modified 800H and the unmodified 800H. The specimens were tested without cold working prior to aging. At both the yield strain and 5% plastic strain the modified 800H alloy exhibits a flow strength superior to that of the unmodified alloy.

Fig. 1 Comparison of yield and 5% plastic strain load relaxation data from laboratory heat modified and unmodified 800H.

Figure 2a shows load relaxation data from the modified 800H and the modified 316 stainless steel (CE3). Both specimens were in the non-cold worked state. At the yield strain the flow curves initially overlap, but then begin to diverge at a strain rate of approximately 10^{-6} s^{-1} with CE3 exhibiting a higher flow strength. This difference is not observed in the data obtained at 5% plastic strain. Each of the curves exhibit the sigmoidal shape characteristic of the contribution of grain boundary sliding to the total deformation.⁴

Figure 2b shows load relaxation data of the modified 800H and CE3 obtained from specimens which were cold worked 5% prior to being tested. These data show qualitatively the same behavior as that in Figure 2.

In Figure 3 load relaxation data obtained from the modified 800H and the modified 800H tube material are compared. These specimens were tested without cold working prior to aging. The flow strength of the laboratory heat material is consistently higher than that of the tube material.

Fig. 2a Comparison of yield and 5% plastic strain load relaxation data from laboratory heat modified 800H and laboratory heat modified 316 (CE3). Both materials received 2% cold work prior to aging.

Fig. 2b Comparison of yield and 5% plastic strain load relaxation data from laboratory heat modified 800H and laboratory heat modified 316 (CE3). Both materials received 5% cold work prior to aging.

Figures 4a (yield strain) and 4b (5% plastic strain) show the effect of cold working prior to load relaxation testing of the modified 800H. These data indicate that a small level of cold work increases the flow strength at all strain rates

A Modified 316 Stainless Steel Alloy with a High Nitrogen Content

Figure 5 presents load relaxation data from the modified 316 stainless steel with a nitrogen content above that in the CE0 material. This material has a flow strength still substantially lower than CE3, which is copper modified.

Fig. 3 Comparison of yield strain and 5% plastic strain load relaxation data from laboratory heat modified 800H and modified 800H tube material.

Fig. 4 Comparison of (a) yield and (b) 5% plastic strain load relaxation data from laboratory heat modified 800H.

Fig. 5 Load relaxation data at yield and 5% plastic strain from modified 316 similar to CE0, but with an increased nitrogen level.

17/14 Cu Mo Reference Alloy

Figure 6 shows a plot of creep strength (flow strength at a strain rate of 10^{-8} s^{-1}) versus aging time at 800°C . The data exhibits a rapid drop from 0 to 200 hrs and then a fluctuation at around 10,000 hrs. As mentioned above, the initial drop from 0 to 200 hrs has been considered to reflect ripening of MC-type precipitates.¹ The fluctuation around 10,000 hrs may, as indicated in the time-temperature-precipitation diagram shown in Figure 7 [ref. 5], reflect the formation of intermetallic precipitates.

Fig. 6 Plot of creep strength versus aging time at 800°C for 17/14 CuMo alloy.

Fig. 7 Time-temperature-transformation diagram for modified 316 stainless steel.⁵

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INEL-2 - CONSOLIDATION OF RAPIDLY
SOLIDIFIED ALUMINIDE METAL POWDERS

R. N. Wright

Idaho National Engineering Laboratory
EG&G Idaho, Inc.
P.O. Box 1625
Idaho Falls, ID 83415-2218

INTRODUCTION

This project will determine the most effective means of, and associated parameters for, consolidation of rapidly solidified powders of alloys based on Ni_3Al and Fe_3Al . The potential advantages associated with rapid solidification processing (RSP) of aluminide powders include fine grain size, improved chemical homogeneity, nonequilibrium degree of ordering, and near-net shape consolidation.

Three consolidation techniques will be explored: hot extrusion, hot isostatic pressing (HIPping), and dynamic consolidation. Extrusion consolidation will be performed by outside vendors and will not include parametric studies of the influence of consolidation parameters on densification. For HIPping studies, effective use of the variables time, temperature, and pressure will be investigated. For the dynamic consolidation studies, the effects of several explosive geometries and shock amplitudes will be examined. Material consolidated using the three methods will be characterized for microstructural stability and mechanical properties. The primary emphasis will be to determine the effects of the consolidation processes on resulting properties.

An initial series of studies have been carried out on powders with nominal compositions of Ni_3Al and $\text{Ni}_3\text{Al}+8\%\text{Cr}$ containing 200 ppm by weight of boron. An additional series of alloys containing additions of iron, and iron and chromium, is currently being examined. The initial studies were conducted using powders produced by centrifugal atomization (CA) and vacuum gas atomization (VGA). The iron containing alloy powders were all produced by VGA. Several VGA powder metallurgy alloys with compositions based on Fe_3Al will be examined using a similar approach and the results will be compared to the Ni_3Al materials.

DISCUSSION OF CURRENT ACTIVITIES

Powder Characterization

Three iron containing alloys are being examined in addition to the original nickel aluminides. The nominal alloy compositions of three iron containing VGA aluminide powders are given in Table 1, along with the compositions of the two alloys previously studied. The compositions of alloys designated 789 and 790 are based on ingot materials developed at Oak Ridge National Laboratory and alloy 794 was selected to investigate the effect of iron additions alone.

All of the VGA alloy powders were generally spherical. Optical micrographs of polished and etched cross sections were examined to determine the nature and scale of the microstructure as a function of the particle size. The solidification microstructures were found to be mixed cellular and dendritic. The nature of the microstructure (i.e., cellular or dendritic) did not vary appreciably with particle size; however, the spacing of the dendrite or cell boundaries increased with increasing particle size as shown in Figure 1. There have been numerous attempts to relate the dendrite arm or cell spacing to the cooling rate based on empirical correlations determined in solidification experiments using pure metals. It is not clear that a simple relationship between boundary spacing and cooling rate should be expected in complex alloys like those studied here. There appears to be a linear relationship between the

Table 1. Composition of Alloy Powders, in Atomic %*

<u>Alloy Number</u>	<u>Ni</u>	<u>Al</u>	<u>Cr</u>	<u>Fe</u>	<u>Mo</u>	<u>Zr</u>
463	77.4	22.6	--	--	--	--
465	73.3	18.4	8.3	--	--	--
789	64.9	17.8	6.8	10.5	--	--
790	63.0	18.5	7.1	10.6	0.7	0.2
794	71.0	18.5	--	10.6	--	--

* All of the alloys contain nominally 200 ppm boron by weight.

Figure 1. Average cell or dendrite boundary spacing as a function of the particle size.

boundary spacing and the particle size for particles in the 10 to 90 μm size range and an apparent saturation in larger particles. An equally important factor seems to be the alloy composition, with the more heavily alloyed powders containing finer microstructures.

The powders were also examined using x-ray diffraction to determine the degree of long range order as a function of the particle size in the as-solidified condition, and in the 50 μm size fraction, as a function of annealing treatments. The Bragg-Williams long range order parameter is shown as a function of the particle size in Figure 2. It is apparent from the figure that the alloy composition influences the amount of quenched in disorder, but for a given alloy the degree of order is independent of the particle size. The effect of alloy composition is consistent with several studies reported in the literature.¹⁻⁴ It has generally been found that the addition of iron or chromium results in quenched-in disorder as evidenced by antiphase boundaries in alloys solidified by melt spinning or atomization. With Ni_3Al of near stoichiometric composition it is difficult to quench in disorder regardless of the solidification rate.

Figure 2. Bragg-Williams long range order parameter as a function of the particle size.

The size of the antiphase domains for the VGA powders was obtained by measuring the x-ray diffraction line broadening from the (100) and (110) superlattice peaks. The x-ray particle size values from the (100) superlattice peaks obtained from the Scherrer equation, which correspond approximately to the antiphase domain size, are plotted as a function of the powder particle size in Figure 3. X-ray line broadening from the fundamental peaks was also measured, and the calculated particle size values were considerably larger than those calculated from the superlattice lines and showed relatively little change with powder particle size. Powder samples that had been annealed at 900°C for one hour in vacuum were used as standards for instrument broadening in all cases. Broadening of the fundamental lines results from defects in the solidification structure such as dislocations and twins, but does not include a contribution from disruption of the long range order in the form of antiphase boundaries. The broadening of superlattice lines contains contributions from both types of defects. The fact that the measured particle size values from the superlattice lines are much smaller than those from the fundamentals indicates that antiphase boundaries are the predominant defect in the substructure.

Figure 3. Particle size values obtained from 100 superlattice x-ray peak broadening.

The data shown in Figure 3 indicate that the antiphase domains increase in size as the powder particle size increases for the alloyed nickel aluminides. It should be noted that the x-ray particle sizes measured from the superlattice and fundamental lines for alloy 463 are approximately equal, indicating that few antiphase boundaries are present. The relative domain sizes correlate with the general trend in the degree of long range order shown in Figure 2; the more highly alloyed powders contain greater quenched-in disorder and smaller domains. The fact that the domain size is a function of the powder particle size, while the long range order parameter is nearly constant, appears to indicate that the quenched-in disorder is in the form of individual wrong-site occupancy in addition to the contribution from antiphase domain boundaries.

Characterization of Hot Extruded Material

Portions of the three iron containing aluminide powders were consolidated by hot extrusion in evacuated steel cans at 1100°C. The microstructures of the as-extruded material showed that alloys 790 and 794 were essentially fully dense, while alloy 789 exhibited some porosity extended in the extrusion direction. Specimens from the extrusions were annealed for one hour at temperatures from 900 to 1200°C, water quenched, and examined using optical metallography. The resulting microstructures showed fine grained equiaxed material, and alloys 789 and 790 had a second phase on many of the grain boundaries that was identified as the martensitic phase. The β' phase has been related to crack initiation during attempts to cold work ingot material with compositions similar to alloy 790; it was therefore of interest to quantify the amount of the phase as a function of annealing treatment. The volume of β' is shown as function of the annealing temperature for one hour anneals in Figure 4. The volume fraction of β' is quite small after the low

Figure 4. The volume fraction of the B_2 NiAl phase as a function of annealing temperature.

temperature anneals and increases to account for a significant fraction of the microstructure after annealing at 1200°C. The volume fraction of β' after annealing at 900°C is likely to be very similar to the value for the as-extruded material. Room temperature tensile properties of the as-extruded material, given in Table 2, indicate that the small amounts of β' do not significantly reduce the ductility. It is also apparent from the table that the mechanical properties of the iron containing alloys are quite good compared to the two alloys considered previously in terms of both room temperature strength and ductility.

The grain size of the extruded materials was measured after annealing for one hour at temperatures from 900 to 1200°C. These values are shown in Figure 5 along with those determined previously for alloys 463 and 465. It can be seen that alloying the binary material significantly retards grain growth. In the alloy containing Cr additions, the grain growth retardation has been found to result from pinning by Cr rich alumina particles at low temperatures and the presence of a disordered phase above 1000°C. TEM results indicate that the iron containing alloys also contain alumina particles at low temperatures and disordered phase at elevated temperature, as well as the β' phase in alloys 789 and 790.

Microstructural development of alloys 789 and 794 has been examined as a function of annealing treatments using TEM. The alloy containing only an iron addition has a single phase $L1_2$ structure after annealing below 1000°C. Above that temperature, a two phase microstructure containing

Table 2. Room Temperature Tensile Properties of P/M Nickel Aluminides

Alloy	Upper Yield Stress (MPa)	Ultimate Stress (MPa)	Total Elongation (%)
463	796	1490	32
465	1086	1600	32
789	696	1321	32
790	850	1465	30
794	702	1372	42

Figure 5. Average grain size of hot extruded materials as a function of the temperature for 1 h anneals.

webs of disordered material within an ordered matrix begins to form. The microstructures formed in the powder metallurgy material are very similar to those reported for ingot material of the same composition.⁵ In alloy 789, which contains both iron and chromium, the microstructural development is somewhat more complicated. After annealing at 900°C the microstructure contains regions of cuboidal ordered domains that are separated by disordered webs, shown in Figure 6a. On annealing at 1000°C the cuboidal ordered domains coarsen into rectangular shapes and the thickness of the disordered regions increases, Figure 6b. Annealing above 1000°C results in the matrix decomposing into regions of order separated by disordered material, and the epitaxial relationship between the ordered and disordered material is lost. Samples that were annealed at 1100 and 1200°C are shown in Figures 6c and d, respectively. This unusual response to heat treatment results in refined microstructures forming at higher annealing temperatures. The driving force for transformation appears to be redistribution of aluminum from the $L1_2$ ordered phase to the aluminum rich β' phase, which increases in volume fraction at the higher annealing temperatures. Preliminary measurements of microhardness suggest that the refined microstructures from higher temperature annealing may result in strengthening. Tensile testing is now under way to confirm this observation.

(a)

(b)

Figure 6. Transmission electron micrographs of the microstructure of alloy 789 after annealing 1 h at (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C.

(c)

(d)

Figure 6. (Continued).

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ORNL-2(B) - DEVELOPMENT AND EVALUATION OF ADVANCED
AUSTENITIC ALLOYS

R. W. Swindeman, G. M. Goodwin, and P. J. Maziasz

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

The purpose of this task is to evaluate advanced austenitic alloys for the design, construction, and reliable operation of heat recovery systems in coal combustion plants through utilization of higher-temperature advanced steam cycle concepts. The approach is to consult with boiler manufacturers, utilities, and related industrial groups to establish the alloy performance criteria. Factors considered will be strength, ductility, corrosion resistance, stability, fabricability, inspectability, and costs. The availability and performance of existing alloys will then be reviewed in comparison with the criteria. We developed a program plan that identifies the needed research to qualify existing alloys, modify existing alloys, or develop new alloys. Concepts in materials science will be used to the fullest extent to select compositions expected to meet the criteria. Industrial subcontractors will supply heats of these alloys, and Oak Ridge National Laboratory (ORNL) and university subcontractors will provide the expertise to screen and evaluate the alloys through experimental work. Exploratory studies of fabrication methods, joining methods, and surface treatments will be undertaken on the most promising alloys. A procedure will be developed whereby the optimum alloy composition and surface treatment can be selected according to the specific performance requirements related to environment, component configuration, fabrication methods, and the load-time-temperature histogram for the component. More details on the project are available in an assessment report¹ and an alloy design criteria report.²

DISCUSSION OF CURRENT ACTIVITIES

Industrial and University Interactions

Small heats of tubing were produced by Combustion Engineering and Babcock and Wilcox³ (see Fig. 1), and a research subcontract has been placed with Babcock and Wilcox to examine methods of surface treating, cladding, and optimization of fabrication schedules for maximum strength in tubing. A research subcontract was placed with the University of Tennessee to select and evaluate filler metals suitable for welding advanced alloy tubing, and another research subcontract was placed with the University of Southern California to produce quantitative metallurgical data on aged material.

Mechanical Properties

To date, over 100 creep tests have been performed on the developmental alloys, and a large number of these tests have exceeded 10,000 h. Early data established that the optimum thermomechanical treatment of both the "lean" stainless steels and the modified alloy 800H required a solution treatment in excess of 1115°C followed by cold or hot working to approximately 10%.⁴ The mill anneal was expected to produce this condition. The testing conditions were expanded for the most promising alloys to a range of temperatures and stresses, and results were summarized in a recent report.⁵ Because of the limited availability of material, however, no large-scale testing was undertaken until the heats of superheater tubing were delivered. Some trends for stress vs time to rupture are indicated in Fig. 2, which shows the log stress vs the Larson-Miller parameter for tests on modified type 316 stainless steels. Data from five heats are included and compared against two lines: the solid line represents the trend for the average strength required to meet the target design strength of 60 MPa at 700°C; the dashed line represents the trend for the minimum strength that must be exceeded. All heats when tested in the hot-rolled or cold-rolled condition exceeded the strength requirements by a wide margin.

Fig. 1. Heavy-wall and thin-wall tubing produced from modified type 316 stainless steel and modified alloy 800.

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Fig. 2. Log stress vs Larson-Miller parameter for rupture of modified type 316 stainless steels.

Figure 3 shows the plots of strength vs temperature for the three developmental alloys. The strength was estimated by the rules of the *ASME Boiler and Pressure Vessel Code*, Sect. I. A comparison is made with 17-14CuMo stainless steel. It appears that the nickel-chromium-iron aluminides have the best strength up to 600°C. Above this temperature, the modified type 316 stainless steel and modified alloy 800H are better.

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Fig. 3. Estimated design stresses for three advanced austenitic alloys and 17-14CuMo stainless steel.

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ORNL-2(E) - FABRICATION DEVELOPMENT OF NICKEL-IRON ALUMINIDES

V. K. Sikka, C. T. Liu, J. V. Cathcart, and J. J. Campbell

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

The purpose of this task is to scale up the melting of nickel-iron aluminide alloys and develop the fabrication technology for various product forms using forging, extruding, and rolling methods. A second purpose of this task is to perform tensile and creep tests on material produced by various processes. This task also includes work to develop high-strength carbide-stabilized nickel-iron aluminide compositions and investigate their welding and corrosion response.

DISCUSSION OF CURRENT ACTIVITIES

Processing Technology Development for Nickel-Iron Aluminides

Melting

The chemistries for nickel-iron aluminide alloys¹ of nominal, low side, and high side of nominal composition were developed for melting studies (Table 1). Each composition was air-induction melted in about 5.9-kg (13-lb) heats and poured into 71-mm-diam graphite molds. After cutting the hot top, each heat yielded a 4.5-kg (10-lb) ingot 178 mm in length. Two ingots were prepared for each of the compositions listed. No problems were encountered during melting of these heats. The surface quality of each ingot was excellent. Based on previous experience, we believe that nickel-iron aluminides should be adaptable to conventional melting techniques such as air induction, vacuum induction, and electroslag remelting.

Table 1. Chemical analysis of nickel-iron aluminide alloys melted in 4.5-kg (10-lb) ingots at ORNL

Element	Nominal composition		Low side of nominal composition		High side of nominal composition	
	(at. %)	(wt %)	(at. %)	(wt %)	(at. %)	(wt %)
Ni	63.0	70.66	64.5	72.06	61.5	69.25
Al	18.5	9.54	18.0	9.24	19.0	9.83
Cr	7.0	6.95	6.5	6.43	7.5	7.48
Zr	0.2	0.35	0.2	0.35	0.2	0.35
Mo	0.7	1.28	0.7	1.28	0.7	1.29
Fe	10.5	11.20	10.0	10.63	11.0	11.78
B	0.1	0.021	0.1	0.021	0.1	0.021

Melting of 227-kg (500-lb) Heat

Based on the experience with melting of 5.9-kg (13-lb) heats at ORNL, a scaled-up heat of 227 kg (500 lb) was melted at Combustion Engineering, Chattanooga, Tennessee. The heat was melted by air induction and poured into a 150-mm-diam ingot. A photograph of the 227-kg (500-lb) ingot after cutting the hot top is shown in Fig. 1. An analysis of the ingot is compared with the target analysis in Table 2. This table shows that all of the target elements were met, and both nitrogen and oxygen contents are extremely low. Based on the results of the 227-kg (500-lb) heat, we believe that the next scale-up to 227-kg (500-lb) heat should be readily possible.

Mechanical Properties

In addition to melting and processing of 5.9-kg (13-lb) heats, the purpose of this study was to evaluate the mechanical property variations of nickel-iron aluminide for nominal, below nominal, and above nominal compositions. Tensile property plots of various compositions are shown in Figs. 2 through 5. The temperature ranges from room temperature to 1000°C. These figures show that the variations in properties between the heats of nominal, below nominal, and above nominal are similar to variations between the two heats of the nominal composition.

Fig. 1. Photograph of pieces cut from 150-mm-diam ingot cast from 227-kg (500-lb) air-induction-melted of IC-357.

Table 2. Comparison of target and check analysis for 227-kg (500-lb) heat of IC-357 melted by air-induction process at Combustion Engineering, Chattanooga, Tennessee

Element	Weight percent	
	Target	Check
C	--	0.022
S	--	0.033
Ni	70.7	69.7
Cr	6.95	6.74
Mo	1.28	1.03
Al	9.54	10.00
B	0.021	0.022
Zr	0.35	0.38
Fe	11.20	11.84
N	--	0.0023
O ₂	--	0.0017

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Fig. 2. Yield strength (0.2%) as a function of test temperature for 5.9-kg (13-lb) heats of nominal, above normal, and below normal compositions of IC-537.

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Fig. 3. Ultimate tensile strength as a function of test temperature for 5.9-kg (13-lb) heats of nominal, above nominal, and below nominal compositions of IC-357.

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Fig. 4. Total elongation as a function of test temperature for 5.9-kg (13-lb) heats of nominal, above normal, and below normal compositions of IC-357.

Fig. 5. Reduction of area as a function of test temperature for 5.9-kg (13-lb) heats of nominal, above nominal, and below nominal compositions of IC-357.

The creep curves (strain vs time) for nominal and below nominal compositions are shown in Figs. 6 through 8. Once again, the spread in the creep strain data due to composition variation is typical of that observed between the repeated tests of the same composition. The stress-rupture data on various compositions is plotted as a Larson-Miller plot in Fig. 9. Similar plots for creep-rupture elongation and reduction of area are plotted in Figs. 10 and 11. These plots show that there is nominal variation in rupture strength and ductility properties between the nominal, below nominal, and above nominal compositions. Results of these studies show that the scale-up for nickel-iron aluminides is possible from both melting and mechanical properties considerations.

Corrosion Behavior of Nickel-Iron Aluminides

Several composition modifications were attempted in order to reduce the previously observed spread in the sulfidation resistance behavior of the nickel-iron aluminide composition of IC-357. The new composition modifications included control of chromium content and additions of

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CREEP PROPERTIES OF IC357 HEATS

Test Conditions: 40ksi 649°C

Ann 1100°C/1h in Quartz

Fig. 6. Creep strain as a function of time at 649°C and 276 MPa (40 ksi) for 5.9-kg (13-lb) heats of nominal and below nominal compositions of IC-357.

ORNL-DWG 88-15100

CREEP PROPERTIES OF IC357 HEATS

Test Conditions: 20ksi 704°C

Ann 1100°C/1h in Quartz

Fig. 7. Creep strain as a function of time at 704°C and 138 MPa (20 ksi) for 5.9-kg (13-lb) heats of nominal and below nominal compositions of IC-357.

ORNL-DWG 88-15101

CREEP PROPERTIES OF IC357 HEATS

Test Conditions: 10ksi 760°C

Ann. 1100 C:1h in Quartz

Fig. 8. Creep strain as a function of time at 760°C and 70 MPa (10 ksi) for 5.9-kg (13-lb) heats of nominal and below nominal compositions of IC-357.

ORNL-DWG 88-15102

CREEP PROPERTIES

IC357 10KG HEATS

Fig. 9. Creep-rupture data for 5.9-kg (13-lb) heats of nominal, above nominal, and below nominal compositions of IC-357.

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Fig. 10. Creep-rupture elongation data for 5.9-kg (13-lb) heats of nominal, above nominal, and below nominal compositions of IC-357.

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Fig. 11. Creep-rupture reduction of area for 5.9-kg (13-lb) heats of nominal, above nominal, and below nominal compositions of IC-357.

silicon content. Compositions and the bar charts showing the sulfidation response are presented in Fig. 12. Tensile and creep properties of the modified compositions are presented in Tables 3 and 4. Figure 12 shows that the IC-407 alloy containing 3 at. % Si exhibits the best corrosion resistance in a sulfur-bearing environment. However, for the optimum mechanical properties, corrosion resistance, and fabricability, a slight modification of the chromium content in IC-357 is recommended. This composition is represented by IC-406. The results of scale-up and properties presented above are expected to be applicable to IC-406.

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ORNL-DWG 88-15105

CORROSION RESISTANCE OF Ni-Fe ALUMINIDES IMPROVED BY SUBSTITUTION OF SILICON OR ADDITIONAL CHROMIUM

ALLOY COMPOSITIONS

IC-No.	Ni	Al	Cr	Fe	Si
357	64.18	18.50	7.00	10.00	(0.75Mo)
405	61.62	18.00	7.99	12.18	
406	60.48	18.00	8.99	12.18	
407	62.09	17.47	6.99	10.10	3.00
408	62.59	17.98	6.99	10.00	2.00

- PLOTS SHOW WEIGHT GAIN AFTER 168 h CAPSULE TESTS AT 871°C
- VARIABILITY OF CORROSION RESISTANCE OF IC-357
- CORROSION RESISTANCE IMPROVED THROUGH THE ADDITION OF Si (IC-407) OR BY INCREASED Cr (IC-405 AND IC-406)
- IC-407 EXHIBITS BEST CORROSION RESISTANCE IN SULFUR BEARING ENVIRONMENTS

Fig. 12. Effect of composition modification of IC-357 on its sulfidation behavior at 871°C.

Table 3. Effect of composition modification of IC-357 on its tensile properties

Alloy	Composition (at. %)	Yield strength (ksi)	Ultimate strength (ksi)	Elongation (%)
<i>Room temperature</i>				
IC-357	7Cr+0.8Mo	84	170	31
IC-405	8Cr	100	190	22
IC-406	9Cr	109	196	24
IC-408	7Cr+2Si	117	271	29
IC-407	7Cr+3Si	122	225	29
<i>600°C</i>				
IC-357	7Cr+0.8Mo	93	138	27
IC-405	8Cr	98	147	23
IC-406	9Cr	102	154	29
IC-408	7Cr+2Si	122	171	20
IC-407	7Cr+3Si	126	180	16
<i>850°C</i>				
IC-357	7Cr+0.8Mo	71	75	15
IC-405	8Cr	71	75	20
IC-406	9Cr	70	73	26
IC-408	7Cr+2Si	57	62	75
IC-407	7Cr+3Si	53	59	51

Table 4. Effect of composition modification of IC-357 on its creep properties

Alloy	Composition (at. %)	Rupture life (h)	Rupture elongation (%)
IC-357	7Cr+0.8Mo	35	23
IC-405	8Cr	67	23
IC-406	9Cr	127	15
IC-408	7Cr+2Si	48	92
IC-407	7Cr+3Si	11	79

ORNL-2(F) - DEVELOPMENT OF IRON ALUMINIDES

C. G. McKamey, V. K. Sikka, C. T. Liu,
J. A. Horton, and S. A. David

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

The objective of this task is to develop low-cost, low-density inter-metallic alloys based on Fe_3Al with an optimum combination of strength, ductility, and corrosion resistance for use as components in advanced fossil energy conversion systems. Iron aluminides near the Fe_3Al composition are expected to be resistant to corrosion and sulfidation in high-temperature fossil energy systems because of their ability to form protective aluminum oxide scales. However, the usefulness of Fe_3Al is limited by low room-temperature ductility ($\approx 1\text{-}2\%$) and their poor hot strength above 600°C . The current efforts of this task focus on using macro- and microalloying to develop alloys with base compositions near Fe_3Al which have improved hot strength and room-temperature ductility, while retaining the oxidation and corrosion properties of the base alloy.

DISCUSSION OF CURRENT ACTIVITIES

Most of this reporting period has been devoted to studying the effect of casting size, fabrication method, rolling schedule, and annealing and quenching procedures on the tensile properties at room temperature. Our first attempt at scale-up produced an extruded bar with excellent surface quality across the entire length. This bar was produced by extrusion with a ratio of 9:1 at 1100°C of a 6.8-kg (15-lb) heat which had been air-induction melted in a ZrO_2 crucible. A 7.5-cm-long piece of the extruded bar was hot forged without cover at 850°C in 10% steps. The forging had excellent quality even after 60% reduction. The forged piece was hot rolled at 800°C to 0.254-cm-thick sheet. Further reduction to 0.076 cm was accomplished by cold rolling with intermediate anneals of 1 h at 800°C .

A different rolling schedule, which was designated roll 4 and was used to produce a finer cold-rolled structure, was used on another piece of the forged casting. This alloy, designated FA-117 and containing six alloying additions, was tested in tension after several different annealing treatments. The results are shown in Table 1. The recrystallization temperature for this alloy was determined to be 950°C for 1 h, so that the stronger samples which were annealed at 850°C were only partially recrystallized. The best ductility achieved was 4.7% in a sample which had been electropolished to remove edge cracks. The use of a different rolling schedule (roll 4), which produced a finer rolled structure before annealing, did not significantly increase strength or ductility.

This same alloy was used to determine the effect of annealing temperature on the room-temperature tensile properties. Figure 1 shows the curves produced after 15-min anneals at various temperatures. All the samples were air cooled. A gradual increase in ductility was achieved with increasing temperature up to 1100°C, while strength levels remained about the same for all test temperatures.

A study was also performed to determine the effect of quench rates on room-temperature tensile properties. Tensile samples of an alloy modified with only three additives were annealed for 15 min at 1100°C, then quenched by various methods. The results are shown in Table 2. Furnace-cooled samples tended to produce low strengths but more ductility, while strengths were increased by faster quenches. Oil quenching produced both higher strength and improved ductility.

These studies seem to indicate that, in order to produce improved strength and ductility, the optimum rolling, annealing, and quenching procedures need to be determined.

Linear expansion coefficients were determined for alloys FA-39B (Fe-30 at. % Al) and FA-109 (modified Fe-28 at. % Al). The curves of the percentage change in length as a function of temperature were the same for both aluminides. Compared to the curve for type 316 SS, the iron aluminides have a slightly lower thermal expansion at temperature below 950°C, but increase more rapidly above 950°C.

Table 1. Room-temperature tensile properties of FA-117

Heat treatment ^a	Yield (MPa)	Ultimate (MPa)	Ductility (%)
1 h/950°C + 5 d/500°C	263.4	402.0	2.0
EP + 1 h/850°C	374.4	484.0	1.9
EM + 1 h/850°C + 18 h/500°C	384.0	606.8	2.8
EM + EP + 1 h/500°C	373.7	617.8	4.7
1 h/850°C + 5 d/500°C ^b	439.4	626.3	3.3
1 h/950°C + 2 d/500°C ^b	319.9	452.3	2.8

^aEP = electropolish. EM = edges machined to remove flaws.

^bRoll 4.

Fig. 1. Effect of annealing temperature on room-temperature tensile properties of an Fe₃Al-based alloy.

Table 2. Effect of quenching on room-temperature tensile properties

Type of quench	Yield (MPa)	Ultimate (MPa)	Ductility (%)
Furnace cool	202.7	502.0	7.2
Water quench	456.4	610.9	4.3
Oil quench	435.8	657.8	7.0

As a result of a meeting of all persons involved in the study of iron aluminide alloys, two specific alloy compositions were chosen for further study and as base alloys for further composition refinement: one was chosen to produce improved room-temperature ductility, the other for improved high-temperature strength. A series of 13 new alloys based on these compositions are presently being fabricated.

OSU 2 - FUNDAMENTAL STUDY OF ALUMINIZING
AND CHROMIZING PROCESSES

P. A. Choquet, E. R. Naylor and R. A. Rapp

Department of Materials Science and Engineering
116 West 19th Avenue
The Ohio State University
Columbus, Ohio 43210

INTRODUCTION

The simultaneous addition of chromium and aluminum to the surfaces of austenitic and ferritic alloys in a diffusion coating process would provide enhanced oxidation and corrosion resistance at high temperatures (700 to 1000°C) in a variety of environments. For ferritic alloys, an external surface composition of about 20-25 wt.% chromium and 4-8 wt.% aluminum would form a protective alumina scale during exposure to an oxidizing environment. For austenitic base metal alloys, simultaneous chromizing/aluminizing will introduce a multiphase coating with a ferritic matrix, which is also an alumina former.

During the six first months, a computer-assisted thermodynamic study of the equilibrium vapor pressures of volatile species formed by the pack components was performed, and some diffusion coatings involving simultaneous chromizing/aluminizing of low and high alloy steels were achieved¹.

Comparable vapor pressures for the chromium and aluminum halides can be generated by using chloride activators and Cr-Al binary masteralloys in the range 85Cr-15Al to 95Cr-5Al. However, fluoride activators generate excessively high aluminum fluoride partial pressures and low fluorine activities even for use with masteralloys having low aluminum activities, so that the vapor pressures for the chromium fluoride species are too low to support chromizing.

Coatings on 2.25Cr-1Mo-0.1C steel and on 304 and 316 stainless steel have been achieved. Two different types of coatings were obtained on 2.25Cr-1Mo-0.1C steel specimens: a high Cr coating surface (Cr content between 20 and 25 wt.%) and an Al-Cr coating ($C_{Al} = C_{Cr} = 10$ wt.%). Raising the temperature resulted in an additional 2.5 wt.% Al to the high Cr coating. In austenitic alloys (304 and 316 SS), a multiphase interdiffusion layer with a ferrite matrix and precipitates of the beta (NiAl) phase increased the Al content in the external zone of these alloys.

During the past six months, the mechanism of growth of the Cr and Al coating on 2.25Cr-1Mo-0.1C steel has been studied in detail, and new masteralloy compositions with different activators have been used to coat 304 and 316 stainless steels.

DISCUSSION OF CURRENT ACTIVITIES

Experimental results of the second six months of the project are summarized below.

Results

Codeposition of Cr and Al into Iron

A pack containing 10% pure Al, 40% pure Cr, 49% Al_2O_3 and 1% NH_4Cl activator powders was used to coat iron at 1050°C for 10 hours. These experimental conditions were indicated by an old patent² which claimed that codeposition of Al and Cr is possible using powdered pure Al and pure Cr.

Figure 1 shows a cross-section of the iron specimen and the corresponding concentration profiles for Al and Cr. An aluminization coating was achieved: 50 at.% Al and 5 at.% Cr at the surface. The presence of any chromium in the coating results from the inclusion and dissolution of Cr pack particles which were entrapped and dissolved into the coating. Indeed, at 1000°C , a liquid phase must also be formed between the Al and Cr particles at the surface of the iron substrate. Interdiffusion between this liquid phase and the substrate could cause the solidification of a thin outer layer with entrapped Cr particles.

This lack of vapor phase chromizing in the presence of Al confirms a thermodynamic study done by Kung and Rapp³, who calculated the composition of the gas in equilibrium with a hypothetical pack containing pure Al and pure Cr powders for various halide activator salts. They showed that because of their high thermodynamic stabilities the partial pressures of aluminum chlorides are several orders of magnitude higher than those for chromium chlorides.

By consequence, Cr cannot be transported simultaneously during Al deposition under these conditions. Indeed, the claim of the Galmiche patent² is invalid, and no experimental evidence was presented to support its validity in the first place.

Figure 1: (a) Cross-section of Fe Sample Coated at 1045C for 10 hours in NH_4Cl activated pack with pure Al and Cr powders (ratio Al/Cr = 1/4), (b) Concentration Profiles for Al and Cr.

Codeposition of Cr and Al into 2.25Cr-1Mo-0.1C Steel

Table I summarizes the weight change, thickness and composition at the external surface for coatings achieved at 1000°C. Six different activators and five different masteralloys were tested.

Masteralloys of 92Cr-8Al or 90Cr-10Al compositions were used to produce coatings with 20 to 30 wt.% Cr, but the Al content stayed below 2 wt.%; these results are highlighted in Table I. Certain conditions in Table I are indicated to form an external Cr carbide layer initially. At 1000 C, relatively unstable activators such as CrCl_2 or FeCl_2 generate high Cl and Cl_2 partial pressures which are favorable for the formation of chromium chloride vapor. However, the formation of HCl from gaseous hydrogen favors high aluminum halide partial pressures; therefore such an environment is an aluminizing agent.

Figure 2 shows the coating compositions as a function of masteralloy composition for various activators. Two different types of coatings have been achieved for each activator with different masteralloy compositions. One type of coating, called type II has a high Al concentration, 8 to 10 wt.% and a low Cr concentration, less than 12 wt.%. An example of a type II coating is shown in Fig. 3. Presumably, type II coatings have good high temperature oxidation resistance but poor hot corrosion resistance due to the low Cr content. Another type of coating, called type I, has a Cr concentration of 20 to 30 wt.% and an Al concentration below 2 wt.%. Consequently, inverse properties can be expected. However, oxidation and hot corrosion testing of these coatings has not yet been performed.

The external surface compositions of the coatings produced using a CrCl_2 -activated pack with 90Cr-10Al masteralloy at various temperatures are summarized in Table II. Temperatures up to 1045°C increase the coating growth rate and the Cr and Al concentrations, and an external Cr,Fe carbide is formed at the surface. However, above 1050°C, the observed negative weight changes indicate that Cr and Al were deposited by the formation and loss of iron chlorides, and no external carbide layer was formed. Above 1050°C, Type I coatings were achieved.

Because of these complex observations, further study of the growth mechanism of these coatings seemed necessary to improve our understanding and the control of coating characteristics. A kinetic study of the formation of the Cr and Al diffusion coating into 2.25Cr-1Mo-0.1C steel using a CrCl_2 activated pack with the 90Cr-10Al masteralloy was performed. A type I coating was obtained. The

Table I: Weight Change ($\Delta m/s$), Thickness (d) and Composition at the External Surface of the Coating on Fe 2.25Cr-1Mo-0.1C Steel Formed at 1273K; Ar Background Gas.

Activator Masteralloy		CrCl_2	$(2)\text{AlCl}_3$ $+(1)\text{NaCl}$	NaCl	NH_4Cl	AlF_3	FeCl_2
		*	*				
<u>95Cr/ 5Al</u>	Cr	25.0	17.0			23.5	
	Al	0.0	0.0			0.0	
	Mo	1.0	1.5			1.5	
	$\Delta m/A$	+26.0	+26.0			-7.7	
	d	100	110			100	
			*				
<u>92.5Cr/7.5Al</u>	Cr		8.5		20.5	16.5	
	Al		7.5		1.5	1.5	
	Mo		2.0		2.0	1.0	
	$\Delta m/A$		-19.0		-1.1	-4.7	
	d		177		123	50	
		*					*
<u>90Cr/10Al</u>	Cr	23.5	7.0	4.0	6.5	3.0	17.0
	Al	1.5	14.0	3.0	9.0	12.0	1.0
	Mo	1.0	1.5	2.0	1.0	1.5	1.5
	$\Delta m/A$	+30.0	-9.0	-10.0	-26.0	+1.0	-5.0
	d	190	314	?	265	300	187
<u>85Cr/15Al</u>	Cr	3.0		3.0	3.5		4.0
	Al	9.0		11.0	14.0		9.0
	Mo	2.0		1.5	2.0		1.0
	$\Delta m/A$	-1.0		+6.7	-25.0		-2.5
	d	325		224	435		294
<u>80Cr/20Al</u>	Cr			2.5	3.0		
	Al			9.5	20.0		
	Mo			1.5	1.5		
	$\Delta m/A$			+2.8	+22.0		
	d			160	437		

(*) Formation of a chromium-iron carbide outer-layer

Figure 2: External Composition of 2.25Cr-1Mo-0.1C Steel Coating at 1000C for various activators as a function of the aluminum concentration in the masteralloy.

Figure 3: (a) Cross-section of 2.25Cr-1Mo-0.1C Steel Coating Formed in NH_4Cl Activated Pack With a 90Cr-10Al masteralloy at 1000C,
 (b) Concentration profiles of Cr, Al and Mo.

microstructure and composition of the coating after 4, 9, 16 and 25 hours were investigated and are shown in Figs. 4 and 5.

During the first 4 hours, a fine outer layer of M_7C_3 carbide (M = Cr, Fe) formed on the surface of the substrate. This layer resulted from the reduction of the $CrCl_2$ vapor at the surface of the specimen to deposit chromium coupled with the migration of carbon from the alloy interior, Fig. 5a. This formation of an external carbide layer during chromizing of C-containing steels is well known in industry. The austenite substrate at the coating temperature suffered decarburization immediately below the coating. Precipitation of Cr-rich carbides at grain boundaries was also observed.

After the first 4 hours of coating, an $M_{23}C_6$ layer grew at the expense of the M_7C_3 layer. During this stage, some chromium was released by the carbide layer to precipitate ferrite in the austenite matrix. After 9 hours, the $M_{23}C_6$ layer partially dissociated and developed porosity which permitted Al and Cr to diffuse to the austenitic substrate, creating a ferritic case. This interdiffusion zone had a depth of 100 microns and a Cr concentration of 20 wt% just below the carbide layer.

After 25 hours, a 150 micron thick coating had developed with a composition Fe-30Cr-3Al at the external surface, (Fig. 5b). The carbide layer was porous. At the carbide layer/ferrite interface, carbides were precipitated at the grain boundaries.

In summary, the use of masteralloys possessing high chromium activities to coat 2.25Cr-1Mo-0.1C steel resulted in the formation of an outer metallic carbide layer during the initial stage of the process. This layer degraded progressively because of Cr absorption and carbon depletion in the ferrite zone. Then Cr and the Al were diffused into the ferrite.

Codeposition of Cr and Al into Ferritic Steels (Fe-12Cr)

Figure 6 shows the microstructure and the concentration profiles for an $AlCl_3$ + NaCl-activated pack with 92Cr-8Al masteralloy at 1323 K for 16 hours. The coating was homogeneous and neither porosity nor internal oxidation were observed. Only a thin porous outer layer rich in chromium surrounds the material. A 25Cr-6Al wt.% composition was achieved at the external surface. Thus, this substrate is particularly

Figure 4: Concentration profiles for Cr, Al and Mo in 2.25Cr-1Mo-0.1C Steel Coated at 1055C for different times (CrCl_2 , masteralloy 90Cr/10Al, Ar).

Figure 5: Cross-section by Scanning Electron Microscopy of 2.25Cr-1Mo-0.1C Steel Coating at 1035C for (a) 4 hours and (b) 25 hours (CrCl_2 activator, masteralloy 90Cr/10Al, Ar).

gas/metal
interface

substrate

50 μm

Figure 6: (a) Cross-section by SEM of Fe-12Cr Steel Coated at 1050C for 16 hours ($\text{AlCl}_3\text{-NaCl}$, 92Cr/8Al, Ar) (b) Concentration Profiles for Cr and Al.

**Table II: Compositions at the External Surface of Coating
on 2.25Cr-1Mo-0.1C Steel with CrCl_2 Activator
at Different Temperatures**

Temperature	1015°C	1035°C	1045°C	1075°C	1080°C
	*	*	*		
Fe w/o	74.0	70.0	69.0	86.5	82.5
Cr	23.5	26.5	27.0	9.5	7.5
Al	1.5	2.5	2.5	5.5	8.0
Mo	1.0	1.0	1.5	1.5	2.0
$\Delta m/A$ (mg.cm^{-2})	+30	+25	-10.0	-1.0	+2.0
k_p ($10^{-3} \text{mm}^2 \cdot \text{h}^{-1}$)	0.3	1.0	1.0	5.0	5.0

(*) Chromium-iron carbide outer layer

well suited for simultaneous chromizing/aluminizing to achieve a Kanthal-like surface composition.

Codeposition of Al and Cr into 304 and 316 SS

Miller et al.⁴ achieved a 200 micron thick aluminized coating on 304 SS using a NaF-activated 95Cr-5Al pack at 1000°C. A 92.5Cr-7.5Al masteralloy with a NaCl activator heated at 1050 C for 27 hours resulted in the coating on 304 SS shown in Fig. 7. Since chloride activators can produce comparable Al and Cr halide partial pressures, this 100 micron thick coating probably contains more Cr than the coating of Miller et al.⁴ An extensive characterization of the compositions of the phases in the interdiffusion zone requires TEM and has not yet been made. Thus far no improvement has been made to the two coatings achieved on 316 SS presented in the last semi-annual report¹. Neither coating was ideal, but both should exhibit enhanced oxidation and corrosion resistance.

Codeposition of Cr and Al into Incoloy 800

Figure 8 shows a 100 micron thick coating on Incoloy 800 after 25 hours at 1050°C. A NaCl-activated, 85Cr-15Al pack was used. This coating was 25 to 40 microns thicker than the coating produced by Miller et al.⁴ The interdiffusion zone is about 75 microns thick while an

Figure 7: 304 Stainless Steel Coated for 27 Hours at 1050C With NaCl Activator, 92.5Cr/7.5 Al Masteralloy, in Ar (400X).

Figure 8: Incoloy 800 Alloy Coated for 27 Hours at 1050C With NaCl Activator, 85 Cr/15 Al Masteralloy, in Ar (500X).

outer beta NiAl layer is about 25 microns thick. Formation of this external NiAl layer, which may be brittle, seems inevitable because of the high Ni content of the substrate.

The gross Cr concentration in the interdiffusion zone drops sharply from 77 wt% at the NiAl interface to 31 wt% at about a 20 micron depth. The Cr concentration then gradually decreases to 20 wt% at the coating/substrate interface. The gross Al concentration gradually increases from 1.2 wt% at the NiAl/interdiffusion zone interface to 10 wt% at the coating/substrate interface. The DOE developmental alloys AX1, AX2, AX3 and AX4 have very similar Cr and Ni contents to Incoloy 800, so coatings on these AX alloys should be possible using similar pack contents.

Future Work

In the next six months, a decarburization of the surface of the 2.25Cr-1Mo-0.1 steel will be attempted. This pretreatment should reduce or eliminate the formation of the initial carbide layer. In that case, Cr should be able to enter the substrate and initiate formation of the ferrite phase, thus allowing Al to enter the coating. A study will also begin to evaluate the possibility of incorporating reactive elements (Ti, Zr, Hf, Y) into the coating to improve scale adhesion. Also, attempts will be made to coat the AX series of DOE developmental steels.

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UI-2 - DEVELOPMENT OF A DESIGN METHODOLOGY FOR HIGH-TEMPERATURE
CYCLIC APPLICATION OF MATERIALS WHICH EXPERIENCE CYCLIC SOFTENING

D. L. Marriott, Department of Mechanical and Industrial Engineering
J. F. Stubbins, Department of Nuclear Engineering
F. A. Leckie, Department of Theoretical and Applied Mechanics*

College of Engineering
University of Illinois at Urbana-Champaign
Urbana, IL 61801

INTRODUCTION

This is the last complete semiannual report to be presented for this project. The full three year program is the subject of a full report which is currently in preparation. The final stages of the program are reviewed in this report.

Work during the past six months has been concentrated in three areas. These are,

1. Continued experimental work on 17-14 CuMo austenitic material, with emphasis on crack growth by fatigue, creep and combined creep/fatigue.
2. Integration of the findings of the project into a coherent design methodology.
3. Continued development of inelastic computational methods using PC-based finite element programs.

DISCUSSION OF CURRENT ACTIVITIES

Studies of Advanced Austenitics

Work so far on this material has been limited to exploratory studies for setting test priorities in a future, more extensive, program.

* now Department Head, Mechanical Engineering, UC Santa Barbara

Fig.1. Summary of Strain/Life Fatigue Data for 17-14 CuMo.

Four basic tests have been carried out.
 Strain controlled LCF tests
 Steady load creep tests
 Fatigue crack growth rate tests
 Creep crack tests.

Strain Controlled LCF Tests

Nine strain controlled fatigue tests have been performed on mill annealed material, including the four tests reported in the previous semiannual report. The specimen geometry, and the test machine are identical to those used in the studies of 21/4 Cr 1Mo steel described earlier. The test temperature in this case was 700 C.

Tests were run under fully reversed saw-toothed waveform at two strain rates of 0.004/sec and 1.4E-5/sec.

Figure 1 shows the results on a strain-life plot. There is an 8-fold reduction in cyclic life in going from the higher to the lower strain rate. This change was accompanied by a transition from transgranular to intergranular fracture. In this respect the material shows typical behavior for austenitic steel at elevated temperature.

Hold time tests are in progress.

Steady Load Creep Tests

All together five steady load creep tests have been performed at 700C, at the same nominal stress of 200 MPa. Three previously reported tests went to rupture and two were interrupted during secondary stage creep.

The results for the tests to rupture are shown in Fig. 2. These consist of two specimens in the mill annealed condition, and one which was solution annealed.

The solution annealed material showed shorter lives (100 to 112 hours) and lower ductility than the mill annealed material.

One creep sample solution was solution annealed, coldworked and aged to simulate the type of treatment suggested by Maziaz, et al. This specimen showed very low creep rates, and the test was terminated after 890 hours because it was progressing so slowly. This is a very significant increase in life compared with the as-received condition.

Fig.2. Summary of Creep Data for 17-14 CuMo.

In all instance metallography performed on the failed specimens showed wedge cracking at grain boundary triple points. So far the interrupted specimens have not been examined.

Fatigue Crack Growth Rate Tests

Three fatigue crack growth rate tests have been conducted at 700C. These tests were performed on 1 inch wide by 1/8inch thick, center cracked plates under a maximum tensile load of 100 lb, and an R-ratio of 0.05. Crack growth was monitored by DC potential drop.

The results of test at three frequencies are shown in Fig. 3. The effect of frequency is typical of materials of this type. At all frequencies, the crack growth rate is correlated well by the elastic stress intensity K .

Examination of the fracture surfaces show transgranular crack propagation in the majority of instances, with about 5% intergranular surface observed in the 0.1 Hz test. Lower frequency tests are in progress.

Creep Crack Tests

Two steady stress creep tests have been performed on the center crack specimen. Crack propagation was monitored by DC potential drop, using the same technique as for the fatigue crack experiments.

The results are shown in Fig. 4, showing the correlation of crack growth with C^* , nett section stress and stress intensity range. There is considerable scatter in the results, which may be a function of inaccuracies in the potential drop method, or it could signify inadequacies in the methods of correlation. Whether the reason is one or the other has yet to be determined. In the event, the amount of scatter is not atypical of results published in the open literature.

Both tests were interrupted when the crack growth reached 0.1 inch. The crack opening angle at this point was close to 80 degrees, which is indicative of very creep ductile material.

Fig.3. Summary of Fatigue Crack Growth Data for 17-14 CuMo.

Fig. 4. Summary of Creep Crack Growth Data for 17-14 CuMo.

Design Methodology for Aging and Cyclic Softening Materials

A method has been developed for dealing with cyclic softening, which is believed to be consistent with the practices of the ASME Code. This method was first presented at the AR&DT Fossil Energy Materials Program Conference held in Oak Ridge, September 1988 [1].

The approach is based on the observation that the stress/strain conditions at a point of local inelastic deformation in a complex component follow a "relaxation locus" which appears to be independent, or at least insensitive, to the detailed constitutive material behavior, and is primarily a function of the component geometry. Furthermore, it has been demonstrated that this locus can be determined by multiple linear elastic finite element stress analyses, by perturbing the elastic stiffness of individual elements [2].

The isocyclic stress/strain relation and the "relaxation locus" can both be plotted on common axes, and their intersection define the equilibrium state, as shown in Fig. 5. It is a matter of judgment as to whether the change of strain between the initial elastic state and the final softened state is considered "local" or generalized plastic deformation. More work needs to be done to define an objective criterion of "localized plastic deformation." An interim definition adopted in this study is whether the relaxation locus is steeper than the Neuber hyperbola, defined as the line on which the product of stress and strain remains constant.

The proposed design procedure does not require the constitutive behavior of cyclic softening to be considered explicitly, for the purposes of primary design. If, on the basis of preliminary analysis, it can be shown that cyclic softening effects will be localized, then the initial monotonic material properties can be used in setting the primary design limits. If this criterion is not satisfied, the fully softened state must be used. This proposed design procedure is a departure from the conventional approach used in the ASME Design Code because, instead of using fixed design limits, these are a function of the expected transient service conditions.

Fig.5. Schematic Description of "Relaxation Locus" Concept.

So far the only softening phenomenon to be dealt with explicitly by this approximate approach is time-independent cyclic softening. However, it appears that the same approach can be extended to deal with more complex, time-dependent softening effects such as thermal aging and combined thermo-mechanical interactions. Before this extension can be made, however, it is necessary to determine the character of thermal softening in materials such as the advanced austenitics, in which such effects are expected. This is the subject of work which was started in the past year to examine the mechanical behavior of 17 Cr 14 Ni Cu austenitic steel.

Development of Inelastic Analysis Methods

This element of the project is concerned with developing practical tools for evaluating complex inelastic effects in tubes, such as local softening due to thermal cycling. It has been demonstrated conclusively that inelastic problems of a nontrivial size can be carried out economically, and this basic work was presented in the previous semiannual report.

Work done in this area during the past reporting period has been concerned with adapting the Owen/Hinton programs to deal with thermal stresses and with a wider range of material constitutive relations than were possible in the original code. While significant progress has been made in this endeavor, it is not yet possible to show any tangible results.

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USC-2 - MICROSTRUCTURAL STUDIES OF ADVANCED
AUSTENITIC STEELS

Judith A. Todd

Department of Materials Science
University of Southern California
Los Angeles, California 90089-0241

INTRODUCTION

Maziasz has recently observed that alloy modifications of stabilizing elements, solid solution elements and phosphorus, which improve the irradiation resistance of 316 type austenitic stainless steels, also significantly improve the elevated temperature creep properties of these steels.¹⁻⁵ The improved creep rupture strengths have been attributed to MC and phosphide precipitate distributions, which are enhanced by deformation of the steel prior to creep testing. The role of the solid solution elements, such as copper, is still under discussion.⁶ The present research aims to (1) characterize the zero stress microstructural evolution during tempering of the reference alloy; (2) determine the effects of prior deformation (5-8% cold work) on the precipitation kinetics; (3) investigate the influence of copper and phosphorus additions on the kinetics of aging, and (4) compare these data with microstructural observations from stress relaxation and creep tested specimens. The microstructural studies will provide a data base for phase optimization in these advanced steels.

DISCUSSION OF ACTIVITIES

The tempering kinetics of alloy AX5 has been studied for both the solution annealed and the solution annealed plus cold worked conditions, for times up to 3000 hours at 800°C and 600°C. Matrix phosphide precipitates and a very few MC precipitates evolved in the

solution annealed material. In contrast, stable MC matrix precipitate distributions were observed after only one hour at 800°C and persisted for 3000 hours in the solution annealed plus cold worked samples. At 600°C the quantity and size of the MC precipitates were significantly reduced for all aging times in the cold worked samples. The transmission electron microscopy observations provide an explanation for the significant improvements in creep rupture strength observed in the advanced alloy compared to 316 stainless steel.

Materials

The composition of alloy AX5, together with those of the commercial and developmental alloys compared in creep tests conducted at ORNL, are listed in Table I.

TABLE I: Chemical Compositions of Austenitic Steels

Chemical Analysis (wt %)															
Alloy	C	Si	Mn	Ni	Cr	Ti	Nb	V	Mo	P	S	Cu	N	B	Co
<u>Creep Tests</u>															
316 ESI	0.059	0.56	1.79	13.18	16.49	<0.01	<0.01	0.02	2.24	0.013	0.020	0.09	0.04	-	-
800H	0.080	0.24	0.90	11.90	19.50	-	-	-	-	-	0.003	0.54	-	-	-
17-14															
CuMo	0.098	0.95	0.83	13.85	16.49	0.21	0.45	0.07	1.96	0.014	-	3.07	0.03	-	-
CE0	0.072	0.41	1.80	16.00	14.20	0.24	0.10	0.57	2.45	0.071	0.007	0.03	0.02	0.005	0.008
CE2															
CE3	0.086	0.21	1.75	16.20	14.50	0.27	0.11	0.56	2.41	0.071	0.008	1.96	0.01	0.005	0.008
AX5	0.076	0.12	2.04	16.20	13.90	0.27	0.15	0.52	2.46	0.024	0.015	0.005	0.02	0.005	0.008
AX7	0.075	0.12	2.05	16.00	14.00	0.18	0.15	0.50	2.50	0.070	-	1.50	-	0.005	0.008
<u>TTT diagrams</u>															
1.4970	0.090	0.46	1.70	15.00	14.60	0.46	<0.05	-	1.25	0.003	0.004	0.07	0.01	0.005	0.013
E 1250	0.100	0.58	6.04	9.46	15.30	-	1.20	0.24	1.02	-	-	-	-	0.007	-

Alloy AX5 was annealed for 1 hour at 1250°C in a high purity argon atmosphere, to ensure that all the stabilizing elements were in solution, quenched, and half the material cold rolled by 5.6%. Transmission electron microscopy (TEM) disc blanks were then removed from both the solution annealed and cold worked materials and were

encapsulated in quartz tubes, back filled with argon. These samples were aged at 800°C and 600°C for times of 1, 10, 300, 1000, and 3000 h respectively. TEM specimens were then prepared by electropolishing in a 7:1 volume ratio of methanol and sulfuric acid at -15°C and 120 mA current. The specimens were observed using a Philips 420 scanning transmission electron microscope and a Philips 400 electron microscope equipped with a field emission gun and an energy dispersive X-ray spectrometer.

Results

Tempering Kinetics of Alloy AX5 at 800°C

The one hour solution annealing treatment at 1250°C resulted in a grain size of approximately 200 μm and the dissolution of virtually all the precipitates. Occasional evidence of an undissolved carbide (0.1 μm in size) associated with dislocation tangles was found in the specimen aged for one hour at 800°C (labelled A in Fig. 1a). Small phosphide precipitates (labelled B in Fig. 1a) and twins (labelled C) were also observed in this sample, with fine MC precipitates located at the incoherent twin boundaries (Fig. 1b). M_{23}C_6 precipitates were observed at grain boundaries (Fig. 1c) with dislocations being punched into both austenite grains. Stacking faults could be observed in regions of higher dislocation density and the Moiré fringe contrast associated with the fault arrowed in Fig. 1d suggests planar MC precipitation in the stacking fault plane.

After 10 hours at 800°C, matrix phosphides with MC precipitates on the associated dislocations were observed (Fig. 2a). Grain boundary M_{23}C_6 precipitates were typically 1 μm in size (Fig. 2b). Figure 2c shows a diffraction pattern of a grain boundary M_{23}C_6 precipitate, cube-cube related to the adjacent austenite grain. This pattern also confirms the presence of MC precipitates in the grain boundary.

The evolution of the phosphide and grain boundary precipitates for aging times of 300, 1000 and 3000 hours is shown in Fig. 3. The

Fig. 1 Alloy AX5, 1250°C, 1 h 800°C

- (a) Undissolved carbide (A), phosphide (B), twins (C)
- (b) MC precipitates at incoherent twin boundaries
- (c) $M_{23}C_6$ precipitate at grain boundary
- (d) stacking fault with planar MC precipitation

Fig. 2 Alloy AX5, 1250°C, 10 h 800°C

- (a) matrix phosphides with MC precipitates on dislocation tangles
- (b) grain boundary $M_{23}C_6$
- (c) diffraction pattern showing $M_{23}C_6$ and MC precipitates

phosphides grow to approximately $1\text{ }\mu\text{m}$ in length, and in all cases are associated with misfit dislocations. Virtually no MC matrix precipitation was observed, except at dislocations generated by the phosphide precipitates and the grain boundary precipitates. M_{23}C_6 were the dominant grain boundary precipitates for all three tempering times, (Figs. 3b, 3d), and were up to $2\text{ }\mu\text{m}$ in size after 3000 hours. Figure 3f shows some of the smaller ($0.05 - 0.10\text{ }\mu\text{m}$) titanium-vanadium-molybdenum containing MC carbides, which were also present at the grain boundaries.

When the one hour solution treatment at 1250°C was followed by 5.6% cold work prior to aging, extensive precipitation of MC carbides was observed on matrix dislocations (Figs. 4a, 4b). No precipitate free zone was observed adjacent to the grain boundaries and MC precipitates formed on extrinsic dislocations in the regions of the grain boundaries between the M_{23}C_6 particles. Energy dispersive X-ray (EDX) spectroscopy and convergent beam electron diffraction analyses identified two types of grain boundary carbides, M_{23}C_6 containing Cr, Fe, Mo and Ni, and MC carbides containing Ti, V and Mo. Analyses of these carbides are presented in Table III. A few, fine phosphide precipitates could be found in the matrix for all aging times.

TABLE III: Analyses of Precipitates

Precipitate		Si	P	Ti	V	Cr	Mn	Fe	Ni	Cu	Nb	Mo
AX5 - CW + 1h $800^\circ\text{C}^{\dagger}$												
matrix	(M)	-	-	-	0.7	16.7	0.6	64.8	16.1	-	-	1.1
M_{23}C_6	(GB)	-	-	0.3	2.0	44.9	-	39.5	7.8	-	-	4.0
MC - Ti/Mo	(GB)	-	-	12.9	10.6	15.7	-	40.0	8.8	-	-	12.1
AX5 - CW + 1000h $800^\circ\text{C}^{\dagger}$												
matrix	(M)	-	-	-	0.2	18.1	-	63.6	16.8	-	-	1.3
M_{23}C_6	(GB)	-	-	0.3	2.3	54.9	-	31.4	5.4	-	-	5.4
MC - Ti/Nb	(GB)	-	-	55.6	-	2.4	-	8.3	1.0	-	23.5	8.8
M_6C	(GB)	-	-	0.6	7.8	28.1	-	23.5	2.6	-	-	37.2

[†] in foil analyses;

Increasing the aging time from one hour to 3000 hours produced

Fig. 3 Alloy AX5, 1250°C, 300, 1000 and 3000 h 800°C

- (a) 300 h, matrix phosphides
- (b) 300 h, grain boundary $M_{23}C_6$
- (c) 1000 h, matrix phosphides
- (d) 1000 h, grain boundary $M_{23}C_6$

Fig. 3 Alloy AX5, 1250°C, 300, 1000 and 3000 h 800°C
 (e) 3000 h, matrix phosphides
 (f) 3000 h, grain boundary MC precipitates

Fig. 4 Alloy AX5, 1250°C, 5.6% cold work
 (a) 1 h 800°C, $M_{23}C_6$ and MC precipitation with no precipitate free zone at a grain boundary
 (b) 1 h 800°C, MC precipitation on dislocations in the matrix

very little coarsening of the matrix MC precipitates as shown in Figs. 4c through 4f. These results are in agreement with those of Kesternich^{7,8}, who showed that TiC precipitates in a 15% cold worked 15Cr-15Ni-0.3Ti steel increased in size from approximately 4 nm after 0.2 h to only 8 nm after 2500 h aging at 750°C. The lattice parameter of the matrix MC carbides, determined from the diffraction patterns of the specimen aged for 3000 h, ranged from 0.428 nm to 0.432 nm (note $a_{VC} = 0.416$ nm, $a_{TiC} = 0.432$ nm). Some recovery of the dislocation substructure was observed in the 1000 and 3000 h aged specimens, but this was insufficient to result in rapid coarsening of the MC precipitates. The grain boundary carbides were again predominantly $M_{23}C_6$ (Figs. 5a, 5b). EDX spectroscopy also identified the presence of grain boundary Ti-Nb MC carbides and Mo-rich M_6C precipitates in the samples aged for 1000 and 3000 h at 800°C. Analyses of these carbides are given in Table III.

Tempering Kinetics of AX5 at 600°C

Representative microstructures of alloy AX5 for 10h, 1000h and 3000h in the solution annealed condition only are presented in Figs. 6a through 6c and in the solution annealed plus cold worked condition in Figs. 6d through 6f. Virtually no matrix precipitation was observed for all aging times up to 3000 h in the solution annealed condition. Extensive grain boundary precipitation was observed for both the 1000 h and 3000 h conditions. The cold worked material contained fewer and finer matrix MC carbides at all aging times, resulting in recovery of the dislocation substructure. Analyses of the matrix and grain boundary precipitates are currently in progress.

Discussion of Results

The tempering kinetics of the 16Ni-14Cr austenitic steel are compared with those for 316 stainless steel and modified austenitic steels in Figures 7 through 9. The time-temperature-transformation (TTT) diagram in Figure 7 was compiled for SA 316 steel by Maziasz

Fig. 4 Alloy AX5, 1250°C, 5.6% cold work
 (c) 10 h 800°C, MC matrix precipitation
 (d) 300 h 800°C, MC matrix precipitation
 (e) 1000 h 800°C, MC matrix precipitation
 (f) 3000 h 800°C, MC matrix precipitation

Fig. 5 Alloy AX5, 1250°C, 5.6% cold worked
 (a) 1000 h 800°C, $M_{23}C_6$, MC and M_6C grain boundary carbides
 (b) 3000 h 800°C, $M_{23}C_6$, MC and M_6C grain boundary carbides

Fig. 6 Alloy AX5, 1250°C
 (a) solution annealed, 10 h 600°C
 (b) solution annealed, 1000 h 600°C

Fig. 6 Alloy AX5, 1250°C
 (c) solution annealed, 3000 h 600°C
 (d) solution annealed, 5.6 CW, 10 h, 600°C
 (e) solution annealed, 5.6% CW, 1000 h, 600°C
 (f) solution annealed, 5.6% CW, 3000 h, 600°C

and McHargue⁴, using data from references 9 through 17. It shows that at 800°C, $M_{23}C_6$ precipitates form at grain boundaries in less than 0.1 h, and are the dominant precipitates until Xh1 phase forms after 100 h, followed by Laves phase (200 h) and sigma phase (1500 h). It should be noted that M_6C precipitation was observed only in the temperature range 600°C to 700°C after approximately 2000 h for 316 steel.

TTT diagrams for stabilized austenitic steels have been developed by Murray et al.¹⁸ for Esshete 1250 steel (Fig. 8) and Padilha et al.¹⁹ for steel DIN 1.4970 (redrawn in Figs. 9a - 9c). The compositions of these steels are given in Table I. Esshete 1250 is a Nb-V stabilized 15Cr-10Ni steel, which was solution treated in the range 1050°C - 1150°C, and which contained grain boundary $M_{23}C_6$ precipitates after approximately 3 hours, (NbV)C matrix precipitates after 30 hours and sigma phase after 3000 hours aging at 800°C. (No indication of any cold or warm work prior to the aging treatments was given.) DIN 1.4970 steel is a 15Cr-15Ni-1.25Mo steel stabilized with titanium and containing 30 - 100 ppm B, and 0.013% Co. Figure 9a shows the TTT diagram for the steel after 25% cold work followed by a solution anneal at 1130°C for 30 minutes. In the temperature range 850°C - 1100°C, the first precipitate to form was M_2B . Kesternich and Meertens⁷ have shown this phase to be $(Cr,Fe)_2B$ with thin film EDX analyses of 78%Fe-21%Cr-1%Mo, and energy loss spectroscopy indicating that boron was the only light element present. At 800°C, $M_{23}C_6$ formed after 0.2 h, followed by M_2B and $(Ti,Mo)C$ after 0.9 h. When the solution treatment of 1130°C was followed by 15% cold work prior to aging, M_2B and $(Ti,Mo)C$ both formed after 0.25 h at 800°C, with $M_{23}C_6$ being reported after approximately 8 hours. Secondary $(Ti,Mo)C$ precipitates were observed after 1 hour in both cases and were stable for 3000 hours at 800°C (Fig. 9c).

The matrix and grain boundary precipitates observed in the present study are summarized in Table IV. $M_{23}C_6$ precipitates were observed at grain boundaries in both the solution annealed and prior cold worked AX5 samples aged at 800°C. This is in agreement with

Fig. 7 TTT diagram showing precipitate phase formation in aged SA 316 as a function of time [4].

Fig. 8 TTT diagram for Esshete 1250 steel [18].

a 25% cold worked plus 1130°C for 0.5 h

b 1130°C for 0.5 h plus 15% cold work

c secondary MC carbide precipitation in heat B, compared with creep tested heat C.

Fig. 9 TTT diagrams for DIN 1.4970 steel [19].

Figs. 7 and 9a, whereas Fig. 9b (15% cold worked) indicates that approximately 8 hours at 800°C are required for $M_{23}C_6$ to nucleate. Grain boundary $M_{23}C_6$ were also observed in alloy CE0 after 6174 h creep test at 700°C. $(Cr,Fe)_2B$ precipitates have not yet been identified by EDX analyses, or their characteristic faulted appearance, in the AX5 samples.

TABLE IV: Summary of Precipitates Observed

Material	T (°C)	time (h)	Solution Annealed		Cold Worked	
			GB	M	GB	M
AX5	800	1	$M_{23}C_6$ (TiVMo)C	Phosphide MC*	$M_{23}C_6$ MC	(TiVMo)C phosphide
	800	10	$M_{23}C_6$ MC	Phosphide	$M_{23}C_6$ MC	(TiVMo)C phosphide
	800	300	$M_{22}C_6$ MC	Phosphide	$M_{23}C_6$ MC	(TiVMo)C phosphide
	800	1000	$M_{23}C_6$ MC	Phosphide	$M_{23}C_6$ (TiNb)C M_6C	(TiVMo)C phosphide
	800	3000	$M_{23}C_6$ MC	Phosphide	$M_{23}C_6$ MC M_6C	(TiVMo)C phosphide

GB = grain boundary; M = matrix; * only at dislocation tangles associated with undissolved or grain boundary carbides.

Although the role of boron in this alloy is not yet clear, Maziasz has noted that boron and phosphorus enhanced MC formation and that carbon and boron decreased Laves phase formation in modified 316 steels^{1,20}.

Matrix precipitation of (TiNb)C or (TiVMo)C carbides was rare in the solution annealed AX5 alloy occurring only at dislocation tangles associated with undissolved or grain boundary precipitates. This is in agreement with Kesternich and Meertens' observations of no intragranular TiC precipitation in DIN 1.4970 steel, unless aging treatments in the temperature range 650°C - 900°C were preceded by

cold work⁷. They concluded that precipitation of TiC was dislocation controlled up to 800°C for 25% prior cold work and 900°C for 15% cold work. Above these temperatures recrystallization was observed together with rapid coarsening of the TiC precipitates. In the present study, the introduction of 5.6% cold work prior to aging the AX5 alloy resulted in a uniform, random distribution of matrix MC on dislocations, with the precipitates resisting coarsening for 3000 h at 800°C.

Kesternich⁸ has measured the TiC precipitate size distributions in DIN 1.4970 steel, solution treated at 1100°C and cold worked 15% prior to aging, for times ranging from 0.2 h to 2000 h at 750°C. The observed time dependence of precipitate growth was smaller than $t^{0.1}$ at aging times beyond 20 h, and could not be explained by: (a) diffusion controlled coarsening ($t^{1/3}$ dependence)²¹, (b) pipe diffusion ($t^{1/5}$ dependence)²², (c) diffusion controlled growth²³ or interface controlled ripening²⁴ ($t^{1/2}$ dependence), (d) interface controlled growth (t dependence)²³, or (e) the dislocation climb model by Silcock and Tunstall²⁵. This led Kesternich to propose the following model, consisting of two mechanisms, to explain the TiC precipitate growth. Firstly a dislocation recovery mechanism, in which dislocation sweeping concentrated sufficient solute to result in TiC nucleation at locations where dislocations interacted or annihilated each other. The locally enhanced solute supersaturation may also provide sufficient driving energy for a short period of rapid interfacially controlled growth. Secondly, once the precipitates have grown large enough to effectively pin the dislocations, dislocation annealing stops and growth of the TiC particles ceases. The decrease in precipitate size as the degree of cold work prior to aging increased, could be explained by the increased density of nucleation sites together with the interfacial reaction limited growth of the TiC precipitates.

Both Ti-Nb MC and Ti-V-Mo MC carbides have been observed at grain boundaries in alloy AX5. After only one hour aging of the cold worked AX5, fine (TiVMo)C were observed at extrinsic dislocations in

the grain boundaries. This agrees with observations by Jones et al.^{26,27}, who showed that grain boundary precipitation of NbC in a 20Cr-25Ni-0.5Nb austenitic steel was favored at extrinsic dislocations and grain boundary topographical defects. They observed that after a 1350°C solution treatment, increasing the degree of cold work (0,5,10%), prior to aging for 0.5 h at 930°C, decreased the mean matrix precipitate size, but increased the mean grain boundary precipitate size. The latter was attributed to the increased density of extrinsic dislocations at grain boundaries. The size variation of precipitates within the same sample was attributed to the variation in density of these defects from boundary to boundary. It should be noted however that, unlike alloy AX5, a precipitate free zone was observed to develop adjacent to the grain boundaries in the 20Cr-25Ni steel. In alloy AX5, fine (TiVMo)C precipitates (5-10 nm) were observed at grain boundary dislocations in the regions between $M_{23}C_6$ particles in the cold worked samples aged for 1 and 10 hours, with larger MC (0.2 μ m) being observed after 1000 and 3000 h aging treatments. The combination of grain boundary $M_{23}C_6$ interspersed with the MC precipitates significantly improved the creep strength of the AX and CE series alloys compared to 316 steel.

In addition to the matrix MC precipitates, the presence of 0.02% P in alloy AX5 results in matrix phosphide precipitation in the solution annealed specimens and a finer distribution in the cold worked specimens. These precipitates may be deleterious for the creep strength, since alloy CE0 and AX7 with 0.07% P and higher densities of phosphides, show shorter creep rupture lives than alloys AX5 and AX8. The phosphide precipitates have complex compositions, incorporating Ti, V, Mo and Nb and reducing the amount of these elements available for MC precipitation. Hence, reducing the phosphorus levels to 0.02% appears important for long term creep strength. It will also improve the weldability of the AX series steels.

The presence of M_6C after 1000 and 3000 h in the cold worked AX5 appeared to have no deleterious effect on the creep rupture proper-

ties. Figure 7 shows that Laves phase develops in 316 steel containing 0.56% Si after approximately 150 h at 800°C. No Laves phase was observed in alloy AX5 (0.12% Si) after 3000 h aging and this was attributed to the lower, 0.12%, Si content and the presence of carbon and boron in this steel. It should be noted that no Laves phase was reported for DIN 1.4970 steel (Figs. 9a, 9b) which had a silicon content of 0.46%, boron levels of 0.003% - 0.01% and carbon content of 0.1%.

Analyses of the tempering kinetics clearly show that by careful control of the stabilizing elements (Ti, V, Nb, Mo), minor elements (Si, P, C), trace elements (B), solute supersaturation, grain size and dislocation substructures, it is possible to optimize the precipitate phases and stabilize the microstructures of the advanced austenitic steels to give improved long term creep rupture lives for the AX series steels.

Summary and Conclusions

1. Grain boundary $M_{23}C_6$ precipitates were observed for aging times of 1 h to 3000 h at 800°C in alloy AX5 in both the solution annealed and solution annealed plus cold worked conditions.
2. Dislocations were required for nucleation of the MC precipitates and virtually no MC was observed in the matrix unless cold work preceded aging. MC nucleated on extrinsic dislocations at grain boundaries.
3. Two compositions of MC precipitates have been identified: a titanium rich MC representing undissolved carbide and a Ti-V-Mo rich MC which precipitated on both matrix dislocations and at grain boundaries during aging.
4. Phosphides were present in the solution annealed microstructures for all aging times. They were finer and more extensive in the cold worked specimens.
5. Grain boundary M_6C precipitates developed in solution annealed and cold worked alloy AX5 after 1000h and 3000 h at 800°C.

6. No boride phase has yet been identified in alloy AX5.
7. Laves phase was not identified in alloy AX5 at 800°C.
8. Stress assisted, enhanced MC precipitation resulted in lower creep strains and significant improvements in creep rupture lives of the AX series alloys compared to 316, 800H and 17-14 CuMo steels.
9. Optimization of the mechanical and creep rupture properties of the AX series alloys can be achieved by careful control of solution treatment temperature, stabilizing element additions, and initial dislocation substructure.

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UTN-2 - INVESTIGATION OF WELDING AND JOINING TECHNIQUES
FOR ADVANCED AUSTENITIC ALLOYS

C. D. Lundin, C. H. Lee, D. K. Aidun and T.P.S. Gill

Welding Research Group
Materials Science and Engineering
The University of Tennessee
Knoxville, Tennessee 37996-2200

INTRODUCTION

This report briefly describes the initial experimental results in the evaluation of the weldability of selected austenitic alloys with potential applications in superheaters/reheaters of advanced steam cycles operating at 700°C and 35 MPa pressure.

Fabrication procedures, especially by welding, must fall within the realm of standard practice in the fossil energy industry and be consistent with the tenets of the ASME B&PV Code. The alloys should be free from hot cracking, reheat cracking, HAZ creep rupture property deterioration, exhibit freedom from embrittlement in long time service, be capable of being joined to other alloys without long time interface effects and the filler metals for joining the alloys should be developed concurrently with the alloy selection investigations.

A significant amount of work has been carried out at ORNL on numerous candidate alloys. The work has involved phase stability, creep rupture property determination and weldability¹. From the mechanical property-microstructural correlation studies, several candidate alloys evolved which exhibited significant potential for the long term stability required, together with the desired creep rupture properties. Weldability studies have shown that several of the compositions were marginal for standard fabrication practices and thus a series of alloy modifications were considered based on elevated temperature properties and weldability.

In order to evaluate the weldability of candidate alloys in detail, it is planned to investigate the following:

- a) base metal weldability response
- b) filler metal development
- c) transition joint behavior
- d) weld metal and HAZ sensitization and IGSCC.

DISCUSSION OF CURRENT ACTIVITIES

During this reporting period (Aug. 1 - Sept. 31), several candidate materials: lean 316 stainless steel unclad and clad with 671, modified alloy 800H, 17-14 CuMo and a reference heat of type 316 stainless steel were obtained from Oak Ridge National Laboratories. The chemistry of these materials is summarized in Table 1. These alloys, with the exception of 17-14 CuMo, were produced in tubular form by Combustion Engineering and Babcock and Wilcox (2.5" OD x 0.27" wall). The Combustion Engineering alloys were centrifugally cast at 5.125" OD x 1.125" wall and then reduced. The 17-14 CuMo alloy is in the as-forged and homogenized condition. The Babcock and Wilcox clad lean stainless steel was co-extruded using alloy 671 powder to produce the clad.

Hot ductility tests on lean 316 (AX6 (CE 3890)) have been completed and are discussed below.

Gleeble Hot Ductility Tests

Hot ductility behavior was evaluated using the Gleeble. The technique provides the tensile properties of any microstructure which may evolve within the HAZ. The hot ductility measured in the simulated samples is normally related to the potential for hot cracking in the HAZ, and this is based on the fact that hot ductility of the HAZ must be adequate to plastically accommodate the weld contraction strains without cracking.

Hot ductility was measured during both the on-heating and on-cooling portion of the thermal cycle. The on-cooling tests were conducted from the zero ductility temperature (ZDT), which was measured

during the on-heating tests. The testing conditions and procedure will be reported in detail in the next progress report.

The hot ductility behavior of the AX6 (CE 3890) is given in Figure 1. For comparison, the hot ductility behavior typical of the AISI 347 and 316 NG (Nuclear Grade, $<0.02\% \text{C}$ and $0.06\text{--}0.12\% \text{N}$) which were previously evaluated at UT² are also given in Figures 2 and 3, respectively.

In each figure, the ductility (percentage of reduction in area) is plotted as a function of test temperatures. The solid and dotted curves correspond to the on-heating and on-cooling behavior, respectively. The vertical bars represent data spread at a given temperature. The absence of a bar indicates that the reduction in area for two or three tests at that temperature is essentially the same.

The lean 316 (CE 3890) and AISI 347 have an almost identical on-heating behavior. The hot ductility gradually decreases over a wide temperature range as temperature approaches the ZDT (200 - 300 F°). However, the on-heating ductility of 316NG decreases within a much narrower temperature range (100 F°). Furthermore, the on-cooling behavior of the lean 316 (CE 3890) and AISI 347 is significantly different from that of 316NG. The latter shows a ductility recovery of approximately 60% of the on-heating ductility within about 150 F° of the ZDT of 2500°F. However, the lean 316 (CE 3890) and AISI 347 show virtually no ductility recovery until the on-cooling test temperature reaches 200 - 300 F° below the ZDT. In this range of temperatures below the ZDT, the ductility recovered is less than 20% of the on-heating ductility. The similarity of the lean 316 (CE 3890) material to AISI 347 suggests that the alloy may be sensitive to HAZ hot cracking.

Future Work

During next reporting period, hot ductility evaluation of the other alloys will be conducted. In addition, Vareststraint hot cracking evaluations will be initiated. Furthermore, metallurgical evaluation of the tested samples will be conducted using analytical electron

microscopy (TEM and STEM) to correlate material's behavior with the microstructural characteristics.

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Table 1
Compositions of Austenitic Alloys

Alloy	C	Si	Mn	Ni	Cr	Ti	Nb	V	Mo	P	S	B	N	Cu
CE 3890 ^a	0.079	0.27	1.77	16.87	14.29	0.21	0.10	0.52	2.27	0.04	0.01	0.006	0.012	0.02
CE 3891 ^b	0.097	0.24	1.93	31.08	20.85	0.29	0.20	0.47	2.01	0.003	0.013	0.007	0.01	0.03
17-14 CuMo	0.098	0.95	0.83	13.86	16.50	0.21	0.45	0.07	1.96	0.014	0.005	0.005	0.025	3.07
671 ^c	0.06	0.10	0.10	8al.	49.01	0.25	-	-	-	-	-	-	-	-

a: Equivalent to Ax6

b: Equivalent to Ax2

c: clad

Figure 1. Hot ductility behavior of AX6 (CE 3890).

Figure 2. Typical hot ductility behavior of AISI 347.

Figure 3. Typical hot ductility behavior of 316NG.

WHC-2 - INVESTIGATION OF ELECTRO-SPARK DEPOSITED COATINGS FOR
PROTECTION OF MATERIALS IN SULFIDIZING ATMOSPHERES

R. N. Johnson

Westinghouse Hanford Company
P. O. Box 1970
Richland, WA 99352

INTRODUCTION

The objective of this program is to develop candidate coatings, using the electro-spark deposition (ESD) process, for the protection of materials in sulfidizing atmospheres typical of fossil energy applications. Coatings of interest include single or multilayer deposits of commercially available hardfacing alloys, as well as custom formulations of metal aluminides, chromium alloys, refractory metals, carbides, silicides, and borides. Materials to be protected include low alloy steels, Alloy 800, and Type 310 stainless steel.

Background

Electro-spark deposition 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. The microstructures produced by ESD can provide exceptional corrosion- and wear-resistance for many materials. Nearly any electrically conductive metal, alloy, or cermet can be applied to metallic substrates.

Further background information on the ESD process is provided in the AR & TD Fossil Energy Materials Program Quarterly Progress Report for the Period July 1 through September 30, 1985, WBS Element HEDL 6.1, and in References 1, 2, and 3.

DISCUSSION OF CURRENT ACTIVITIES

During the first phases of this program, ESD coatings were developed using commercially available hardsurfacing materials such as the various iron-, nickel-, and cobalt-base alloys used in wear and corrosion applications, and chromium and chromium carbide. Corrosion tests conducted at ANL (yet to be completed) so far show that the chromium carbide is the best performing material, with a sulfidation resistance nearly 4 times better than Type 310 stainless steel at 875°C.

Most of the commercial electrodes, however, are designed for more general purpose welding or hardfacing applications. While some appear moderately resistant to sulfidation attack, most commercial alloys also contain elements or structures that may be undesirable for fossil energy applications. We are now entering a new phase of the program with the successful development of our capabilities to fabricate customized electrode compositions using vacuum hot pressing of metal and cermet powder compacts. This allows us to investigate materials containing only those elements of interest and to eliminate those believed to be deleterious. At the same time, the ESD process with its tolerance for a wide variety of materials, allows us to use compositions that cannot be successfully applied by most other welding processes.

Selection of materials for the new electrodes is based upon earlier work at WNC and in other portions of the Fossil Energy Program. The most sulfidation resistant materials, for example, usually contain Al (or aluminides), or Cr, or Si, or spinels such as MgAl_2O_4 .

When a given electrode composition is used in the ESD process, the resulting surface coating is an alloy mixture of the substrate material and the electrode material. Subsequent ESD layers can be used to create a coating approaching the electrode composition. This allows a variety of surface alloys to be created from a given electrode/substrate combination by control of deposition parameters and coating thickness.

The first group of custom electrode compositions we have produced are a series of chromium-based alloys with additions of aluminum, spinels, or silicides. Compositions (in weight %) produced so far are:

Cr - 5 Mg Al₂O₄
 Cr - 20 Mg Al₂O₄
 Cr - 50 Mg Al₂O₄
 Cr - 10 Cr₃Si₂
 Cr - 50 Cr₃Si₂ - 7 Al
 Cr - 7 Cr₃Si₂ - 4 Al
 Cr - 25 Al

Other electrode compositions in development include iron aluminide based materials, hafnium carbide cermets, and titanium diboride or zirconium diboride with refractory metals. Substrates of interest include 2-1/4Cr-1Mo steel, Type 310 stainless steel, modified 316 stainless steel, and modified Alloy 800.

The new electrode compositions are being evaluated for coating quality and characteristics, deposition rates, and transfer efficiency. When appropriate deposition parameters are developed, candidate coatings will be selected for further evaluation in corrosion and erosion tests at ANL.

ESD coatings of refractory metals also are being developed for use as diffusion barriers between the substrate steel and another corrosion or erosion resistant coating. Niobium has been applied effectively and produces a hard intermetallic Nb-Fe-Cr or Nb-Fe-Ni-Cr layer (depending on substrate alloy) that may be useful, but also is prone to stress relief cracking. ESD coatings of rhenium on austenitic stainless steels, however, are completely free of cracking and parameters have been developed that produce an excellent, uniform coating. Experiments are now proceeding with the use of rhenium as an initial layer on 310 stainless steel, with subsequent layers of niobium and other corrosion resistant alloys.

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PART IV - CORROSION AND EROSION OF ALLOYS

ANL-3(A) - CORROSION AND MECHANICAL PROPERTIES OF ALLOYS
IN FBC AND MIXED-GAS ENVIRONMENTS

K. Natesan and J. H. Park

Argonne National Laboratory
Materials and Components Technology Division
Argonne, Illinois 60439

INTRODUCTION

The purposes of this task are to (1) evaluate mechanisms of oxidation, sulfidation, and breakaway corrosion for chromia- and alumina-forming alloys exposed to mixed-gas atmospheres that span a wide range of oxygen and sulfur partial pressures typical of both combustion and gasification systems, (2) develop an understanding of the role of several microalloy constituents (e.g., Zr, Nb, Y, Ce) in the oxidation/sulfidation processes, (3) characterize the physical, chemical, and mechanical properties of surface oxide scales that are resistant to sulfidation attack, and (4) evaluate the role of deposits such as FBC sorbents containing sulfur and/or chlorine and ash constituents in the corrosion behavior of metallic alloys and selected coatings.

DISCUSSION OF CURRENT ACTIVITIES

During the current period, laboratory oxidation tests have been continued on model base alloys such as Fe-25 wt.% Cr, Fe-25 wt.% Cr-20 wt.% Ni, and Fe-25 wt.% Cr-6 wt.% Al in the temperature range of 500 to 700°C. Oxidation tests are also in progress on alloys modified by (a) alloying additions of 3 wt.% Nb or Zr, (b) Nb implantation, and (c) sputter deposits of silicon. Thermogravimetric tests are continuing in air and in low- p_{O_2} environments established by means of a 1 vol.% CO-CO₂ gas mixture. The weight change data from a number of these tests were discussed in an earlier report.¹ Several of the exposed specimens were examined by scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) techniques. Figure 1 shows SEM photographs of surfaces of Nb-implanted Fe-25Cr alloy before and after exposure to air for different

times at 700°C. The acicular oxide morphology observed after 5- and 20-h exposures disappeared and became more spheroidal after longer exposure time, as can be seen in the photograph taken after a 170-h exposure. Even though the weight change data showed no effect of Nb implantation on the oxidation rate, the microstructures of Nb-implanted specimens predominantly indicated almost pure Cr_2O_3 scale even after exposure in an air environment. In contrast, scales that develop in Fe-25Cr alloys (without Nb implantation) exposed to air generally contain a significant amount of iron. The absence of iron in scales developed in Nb-implanted specimens can be beneficial in that the sulfidation of base metal element at the gas/scale interface will be delayed, and the time required to initiate breakaway corrosion will thereby be extended.

Fig. 1. SEM Photographs of Nb-implanted Fe-25Cr Specimens in the As-implanted Condition and after Exposure in an Air Environment at 700°C.

Figures 2 and 3 show AES analyses of specimens in the as-implanted condition and after exposure to an air environment for different times. The niobium profile in the as-implanted specimen as a function of sputtering time indicates that the peak niobium concentration occurs beneath the surface of the specimen. At present, calibration runs are being conducted in an Auger unit to correlate the sputtering time with the sputtering rate to arrive at depth profiles. Additional experiments are under way to substantiate the effects of niobium on the growth/breakdown of surface scales.

During the current period, experiments have been carried out to determine the electrical conductivity of thermally grown oxide scales and chemical diffusion of defects in the scales as a function of oxygen partial pressure, temperature, and sulfur level in the gas phase. A gas-tight electrochemical cell (shown in Fig. 4) was used for the measurements of electrical conductivity. The cell consists of two identical yttria-stabilized zirconia (YSZ) disks. The top disk of the cell serves as an oxygen sensor and the bottom disk is used as an oxygen pump. The cell walls consist of several 1.27-mm-diam rings of high-purity alumina which are separated from each other and the disks by thin Pyrex glass. Both YSZ disks were painted with platinum paste on the entire outer face and on that part of the inner face which would be within the enclosure. These electrodes were prepared by heating to a temperature of 980°C overnight. Platinum wires, 125 μ m in diameter, were used as electric leads in the sealed cell. The entire cell was placed in the furnace and a spring force was applied on the assembly to partially seal the cell. A 3% O₂-Ar gas mixture was passed over the cell assembly while firing the cell at temperatures up to 1000°C. During firing, the Pyrex glass (with a softening temperature of 820°C) melted and provided a gas-tight seal. Before the cell was used in conductivity measurements, it was checked for leakage by switching the gas mixtures from air to pure oxygen, and tested via coulometric titration by comparing the oxygen concentration increase based on the cell volume with that calculated from the measured cell voltages.

Fig. 2. AES Analyses of Nb-implanted Fe-25Cr Alloy Specimens in the As-implanted Condition (Top) and after 5 h of Exposure to Air at 700°C (Bottom).

Fig. 3. AES Analyses of Nb-implanted Fe-25Cr Alloy Specimens after 20-h (Top) and 170-h (Bottom) Exposures to Air at 700°C.

Fig. 4. A Gas-Tight Electrochemical Cell Assembly.

The initial conductivity measurements were performed on several different Cr_2O_3 samples. The oxide samples were prepared by (a) in-situ oxidation of Cr metal, (b) complete oxidation of sputter-deposited Cr, (c) complete oxidation of thin Cr foils, and (d) sintering of Cr_2O_3 powder material. Four-probe conductivity measurements were made over a wide temperature and p_{O_2} range with the gas-tight YSZ electrochemical cell. Results for the pure Cr_2O_3 (formed from a completely oxidized thin foil of

Cr) are shown in Fig. 5. The data indicate p-type conductivity behavior for the oxide over the entire p_{O_2} range of the investigation. The experimental measurements are presently being extended to oxides that develop on binary and multicomponent alloys.

Additional experiments are under way to determine the solubility and diffusion of sulfur in thermally grown chromium oxide at relatively high oxygen partial pressures and low sulfur partial pressures, the region in which formation of chromium sulfide is thermodynamically unfavorable. Since sulfur diffusivity and solubility in the oxide scale will be measured by using several sulfur-containing gas mixtures, an open cell that enables switching of gas mixtures (rather than a gas-tight sealed cell) is desired. An open cell, shown in Fig. 6, has been constructed in which the oxide sample and the setup for conductivity measurements are similar to those in the gas-tight cell described earlier. To date, the cell has been used in a purely oxidizing environment (without sulfur) and the results have been compared with those obtained in a closed cell. Figure 7 shows the results obtained for Cr_2O_3 scale with both types of cells. The open-cell data obtained in an air environment agree well with those obtained in a sealed cell. The open cell will be used in the near future to evaluate the effect of sulfur in the gas phase on the conductivity, defect structure, and transport properties in thermally grown oxide scales.

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Fig. 5. Electrical Conductivity of Thermally Grown Cr_2O_3 Scale as a Function of p_{O_2} and Temperature.

Fig. 6. Schematic of an Open Electrochemical Cell for Measurements of Conductivity in Oxygen-Sulfur Environments.

Fig. 7. Temperature Dependence of the Electrical Conductivity of Thermally Grown Cr_2O_3 Scale Determined in Both a Sealed Cell (Solid Symbols) and an Open Cell.

ANL-3(B) - SURFACE MODIFICATION FOR EROSION/CORROSION

C. C. Cheng and G. R. Fenske

Argonne National Laboratory
Materials and Components Technology Division
Argonne, Illinois 60439

INTRODUCTION

The combination of low oxygen pressure, relatively high concentrations of sulfur compounds, and high operating temperatures provides a favorable environment for corrosion and erosion/corrosion of metallic components in coal gasification systems. In coal gasification systems, high oxygen pressure does not exist within the gasifier or downstream components, except in the immediate region of the oxygen injection parts of the gasifier. Equilibrium calculations, based on pressure and temperature, suggest that the free-oxygen pressures are in the range of 10^{-15} to 10^{-20} atmospheres at temperatures ranging from 600°C to 1000°C. In these systems, gaseous sulfur species serve as the second major oxidant. A variety of sulfur species can exist, but hydrogen sulfide (H_2S) and carbonyl sulfide (COS) are the principal sulfurous constituents. Equilibrium calculations suggest that, depending on the sulfur content of the coal, the sulfur pressures of gasification environments are in the range of 10^{-5} to 10^{-10} atmospheres. The presence of these sulfur compounds, and the dual oxidation system they produce, differentiate coal gasification environments from the atmospheres present in heat-treating and most other current commercial processes.

The chemical and mechanical properties of coatings depend strongly on the structure of the coating; in particular, the grain morphology and the structure of the substrate/coating interface. Therefore, microstructural studies of coatings are necessary for an understanding of film formation kinetics and the resulting performance in aggressive environments.

Transmission electron microscopy (TEM) is the best tool for studying the microstructure of thin coatings, which often possess small grain sizes and large numbers of crystalline defects. Optical and scanning electron microscopy often have an insufficient resolution and when using the X-ray

diffraction technique, it is difficult to separate the grain-size and defect contributions to the X-ray peak broadening. TEM observations are most commonly performed with the electron beam normal to the plane of the film. Because the coating microstructure changes during film growth, cross-section TEM studies give a more complete picture of the film structure and also allow imaging of the coating/substrate interface. Thus it is possible to study the relationship between the coating and substrate microstructures. This is especially important for ion-assisted deposition (IAD) because the grain size and the relationship between the substrate and coating at the interface are strongly influenced by the energetic ions.

The advantages of IAD processes include the ability to modify the microstructure and improve the adhesion of coatings. The type of microstructure and the degree of adhesion are dependent on a number of IAD process parameters, including the incident ion energy, the ion/vapor arrival rate, and the deposition temperature. A series of Cr depositions was therefore performed to investigate the effects of these parameters on the microstructure of the deposited coatings and the structure of substrate/coating interfaces, which is of crucial importance for the reliability of the component in oxidation/sulfidation environments.

DISCUSSION OF CURRENT ACTIVITIES

Figures 1 and 2 show cross-sectional TEM micrographs of IAD Cr films deposited at room temperature with 1000- and 100-eV Ar ions, respectively. The ion/vapor arrival rate was approximately 0.5 nm/s, and the Cr vapor deposition rate was -0.4 nm/s. Figure 3 shows a TEM micrograph of a PVD Cr film deposited at room temperature at a Cr vapor deposition rate of 0.4 nm/s. The microstructure of the PVD film is columnar in nature and grain boundary porosity is present in the form of long, narrow pores. Grain boundary porosity is also present in the IAD film produced in the 1000-eV Ar run (Fig. 1), but not for the 100-eV Ar run shown in Fig. 2. (Although grain boundary porosity is absent in Fig. 2, as is typical for regions near the substrate interface, some porosity was observed in regions near the surface of the film.) It should also be noted that the porosity in Fig. 1 for the 1000-eV Ar run is much coarser than that

observed for the PVD film in Fig. 3. Thus, use of the IAD process can result in less grain boundary porosity than one normally obtains in PVD films, but in order to achieve this reduction, it is necessary to deposit the film with low-energy ions.

However, a narrow gap can be observed at the substrate/coating interfaces of the 100-eV-Ar IAD specimens (Fig. 2) as well as the PVD specimens (Fig. 3). The detachment of deposited films indicates that adhesion might be a problem for coatings deposited by PVD and IAD with low-energy ions. Figure 1 shows that the IAD Cr film deposited by 1000-eV Ar adheres well to the substrate. Thus, use of the IAD process can result in enhanced adhesion of deposited films, but in order to achieve this enhancement, it is necessary to deposit the film with high-energy ions.

This is the final report for the ANL-3(B) project, which terminates at the end of this period.

Fig. 1. Cross-sectional TEM View of an IAD Cr Film Bombarded by 1000-eV Ar Ions.

Fig. 2. Cross-sectional TEM View of an IAD Cr Film Bombarded by 100-eV Ar Ions.

Fig. 3. Cross-sectional TEM View of a PVD Cr Film.

BCL-3 - INVESTIGATION OF THE EFFECTS OF MICROALLOY
CONSTITUENTS, SURFACE TREATMENT, AND OXIDATION CONDITIONS
ON THE DEVELOPMENT AND BREAKDOWN OF PROTECTIVE OXIDE SCALES

I. G. Wright, J. A. Colwell,
D. R. Baer* and J. T. Prater*

BATTELLE
Columbus Division
505 King Avenue
Columbus, Ohio 43201-6293

INTRODUCTION

The intended operating conditions of the alloys studied in this program are the temperature range of 500 to 700°C, in environments representing those encountered in projected combustion or gasification processing. In this temperature range the thermodynamic driving forces and the relative kinetics of the competing corrosion reactions will be significantly modified from those occurring in the 1000 to 1100°C range, from which much of the current mechanistic understanding of microalloying effects were derived. It is therefore likely that the mechanisms of oxide formation and growth, and the effects of microalloying constituents will be quite different from those normally thought of for alloys designed to form protective chromia-based or alumina-based oxide scales.

The objectives of this program are (1) to gain an improved understanding of the effects of alloying constituents present at low levels on the development and mode of breakdown of protective oxide scales in conditions representing those encountered in combustion and gasification processes at 500-700°C, and (2) to achieve better control over the growth of scales which will contribute to improvements in long-term, high-temperature corrosion resistance of heat exchanger and heat recovery materials.

* Battelle-Pacific Northwest Laboratories

DISCUSSION OF CURRENT ACTIVITIES

During this reporting period, studies have continued on the initial stages of scale formation on the three master alloys, and on exposures in an $H_2/H_2O/H_2S$ gas mixture chosen to allow screening of the magnitude of the effects of microalloying additions on alloy behavior under sulfidizing conditions.

Early Stages of Oxidation

Specimens of the three master alloys were exposed to the $H_2/H_2O/H_2S$ gas mixture ($P_{O_2} = 10^{-20}$ atm, $P_{S_2} = 10^{-8}$ atm) at $700^\circ C$ in a furnace that was located in a nitrogen-filled glove box, and were then transported from this furnace in a sealed cell to an Auger electron spectroscopy (AES)/X-ray photoelectron spectroscopy (XPS) analytical chamber for analysis. Results from the analysis of specimens exposed for 15 minutes, 24 and 96 hours are summarized in Table 1. Note that in these data, the reported levels of aluminum, silicon, and carbon are probably derived from impurities deposited on the specimen surfaces either during handling or during the analyses. The data suggest the the Fe-25Cr master alloy has formed an essentially Cr-rich oxide film after 15 minutes exposure, and that the Cr content of this film increases only slightly with increasing time. Note that the film, after 15 minutes, contains small levels of Fe and S, and that after 24 hours the Fe content is significantly reduced and is absent after 96 hours, while S was not detected in the films after 24 and 96 hours.

The chromium level in the oxide film formed on the Fe-25Cr-20Ni alloy was significantly lower than that measured on the Fe-25Cr alloy, and apparently did not increase with time up to 96 hours, whereas the Fe content of this oxide film was significantly higher than on the Fe-25Cr alloy and appeared to increase slightly with time up to 96 hours. Sulfur was detected in this oxide film at all the exposure times investigated and, while Ni was detected in the film formed after 24 hours, only a trace of Ni was detected after 96 hours. The two data points for 24 hours represent analyses of different areas, labeled in Table 1 "Spalled

Area" and "Non-Spalled Area". The non-spalled area apparently contained a significant amount of S, probably as an Fe-rich sulfide, while the other area apparently contained Cr and Fe oxides, together with some level of S.

The scale formed on the Fe-25Cr-6Al master alloy showed a rapid increase in aluminum content with increasing time. Note that after 15 minutes the scale contained significant levels of Fe and Cr with small amounts of sulfur, and that the levels of all three elements decreased somewhat with increasing exposure time.

The corresponding transmission electron microscopy (TEM) data obtained from these specimens after exposure for 15 minutes, are presented in Table 2. Note that oxygen is not detected by this technique, and that the scale compositions have been normalized to 100 percent, while ignoring any oxygen content. The structure of the scale formed on the Fe-25Cr master alloy was essentially a hexagonal mixed FeCr oxide, in which the Fe content was roughly 1/10 that of the Cr, and which apparently contained small amounts of Mn and S. The grain size of this film was generally less than 1,000 angstroms. Over the metal grain boundaries, the oxide film was often thickened, as shown in Fig. 1, but had the same composition as the uniform film. There were also patches of thicker oxide or particles within the uniform regions; some of these were enriched in Fe, while others showed significant Al concentrations. The Al-rich particles are thought to be artifacts.

The oxide film formed after 15 minutes on the Fe-25Cr-20Ni master alloy was found to be a mixture of approximately equal parts of the hexagonal Fe-Cr oxide, and the Fe-Cr-Ni spinel. The ratio of Cr to Fe was approximately 3:1, compared to approximately 2:1 indicated by the XPS data. The film also contained a small amount of Ni with traces of Mn and S. The grain size of this film was, in general, <500 angstroms. Thicker patches or particles within the uniform regions of the film were sometimes found to be enriched in Fe, while others showed significant concentrations of Al; again, the Al-rich particles are thought to be artifacts. Figure 2 is a TEM micrograph of an area of this film.

Figures 3 and 4 are TEM micrographs of the oxide film formed on the Fe-25Cr-6Al alloy after 15 minutes and 96 hours exposures, respectively. After 15 minutes, the film comprised hexagonal Cr-Fe oxide and the Fe-Cr-Al spinel in which the Fe-Cr-Al ratios were approximately 4:2:1. After 96 hours, the scale was essentially a mixture of alpha-alumina and the Fe-Cr-Al spinel; in this film the Fe-Cr-Al ratios were approximately 0.4:0.7:1. The grain size of the film formed after 15 minutes was <300 angstroms, and it contained thicker patches or particles within the uniform regions. Some of these thicker patches were enriched in Fe or Cr, while others were highly enriched in Al; the Al-rich particles are thought to be artifacts. After 96 hours, the grain size of the film was <1,000 angstroms, and thicker patches within the uniform regions were enriched in Cr (up to 60 percent) compared to the areas of thin oxide. Thick Cr-rich particles (up to 74 percent Cr) were commonly observed in the film; whether these were located above or below the alloy surface could not be established.

Kinetic and Morphological Characterization Data

Figure 5 shows the isothermal oxidation kinetics of the Fe-25Cr-20Ni master alloy in the $H_2/H_2O/H_2S$ mixture at 700°C. These have been revised since the last semi-annual report by the addition of further data points. As before, the alloy appears to be capable of two types of oxidation behavior in this gas mixture, and the possible rate constants associated with these two modes are indicated in the figure. Each of the data points in Figure 5 is identified with the run number, for instance, C4, and the individual specimen number, for instance, 120. Figure 6 shows the weight gains for the various alloys based on the Fe-25Cr-20Ni master alloy. Data for three separate exposure periods are shown, these being for 526, 1102, and 2102 hours, at 700°C in the $H_2/H_2O/H_2S$ gas mixture. The weight gains for the master alloy after each exposure period are also shown; note that master alloy specimens C4 and C5 exhibited the slower form of kinetics, as shown in Fig. 5, while specimen C3 exhibited the faster form of kinetics. Overall, it appears from the weight gains of all the alloys in run C5 that the corrosion conditions here were less

severe than in the other two runs. After 526 hours, none of the alloying additions made by conventional casting showed smaller weight gains than the master alloy. After the longer exposures, all of the additions resulted in weight gains of a similar or smaller magnitude to the master; the apparently large weight gains for the 1 percent Al and the 1.5 percent niobium-carbide additions after 2102 hours are meaningless because both specimens exhibited through-thickness cracks.

Figure 7 is a similar plot for the powder metallurgically-produced alloys based on the Fe-25Cr-20Ni master. In this case, the D1 and D2 master alloy specimens exhibited the rapid form of kinetics, as shown in Fig. 5, whereas the D3 specimen of the master alloy exhibited the slower form of kinetics. The possibility exists, therefore, that the corrosive conditions during run D3 were somewhat less severe than in the other runs. Note that all the powder metallurgically-produced alloys exhibited smaller weight gains than the master alloy after all three exposure periods. The additions that showed the greatest reduction in weight gain were 2 and 6 percent silicon, and yttrium added as yttria.

Figure 8 represents an attempt to display the relative effectiveness of the various additions and alloying routes by presenting the weight change relative to the weight change of the master alloy exposed under the same test conditions. The percentage weight change was calculated from the weight change of the alloy minus the weight change of the master under the same conditions, divided by the weight change of the master; where an alloy gained less weight in a given test than the master alloy, the value of the percentage relative weight change will therefore be negative in Fig. 8. Similarly, if an alloy shows a negative weight gain, typically because of scale spallation, this will also be represented as a negative value in Fig. 8; comparison of Fig. 6 with Fig. 8 indicates that there are three cases where the negative value in Fig. 8 is the result of scale spallation. These are for the cast 2 percent manganese alloy after 500 hours, and the 2 and 6 percent silicon alloys made by powder metallurgy, after 500 hours. Note also that the high relative weight gain of the cast 1 percent Al alloy and the cast niobium carbide alloy after 500 hours are artifacts due to the specimens being cracked.

Overall, the additions which were observed to consistently provide a significant improvement in the corrosion resistance of the Fe-25Cr-20Ni master alloy (significant meaning around -100 percent relative weight change compared to the master alloy) are additions of 2 and 6 percent silicon added by rapid solidification techniques and 2 percent yttrium added as yttria via powder metallurgy. Other additions which led to significant improvements are the 0.1 and 1 percent yttrium added by rapid solidification, 3 percent silicon added by conventional casting (only after 2000 hours) and niobium carbide added via rapid solidification. The additions of 0.1 and 1 percent yttrium and 1 and 3 percent silicon added via conventional alloying all resulted in higher relative weight gains compared to the master after 500 hours, and lower relative weight gains after 2000 hours. This trend is also supported by 1100-hour data.

Figure 9 represents an attempt to quantify the changes in scale morphologies of some of these alloys as a function of exposure time. Using the five types of scale morphologies identified in the previous semi-annual report, the length of surface occupied by each of the scale types present on a single cross-section of each specimen was measured using a Hurlbutt counter, and converted into the percentage of the length of surface occupied by each scale type. These data are presented as percentage scale type in the diagrams in Fig. 8, and are intended to allow a comparison to be made of the way in which the scale morphologies change with time as a function of alloy addition.

The diagram for the Fe-25Cr-20Ni master alloy, which corresponds to specimens which exhibited the slower form of kinetics, indicates that Type 0 scale, an essentially uniform, protective scale, was formed after 164 hours exposure, but that after 527 hours approximately 30 percent of the surface was covered with the thicker, non-protective scale types which contained sulfide species. The scale morphology after 1104 hours was apparently little changed from that after 527 hours.

The 2 percent silicon addition made by rapid solidification processing resulted in essentially single-phase, thin, protective scales after 1102 and 2101 hours exposure, as did the 6 percent silicon addition made by the same route, although the scale on this alloy contained a few percent of sulfur-containing nodules. The scale formed after 474 hours of exposure

on the 1 percent yttrium alloy made by rapid solidification processing was predominantly Type 2, which is a multilayer, thin, essentially protective scale with small FeS protrusions along the outer edge. After 1102 hours, the scale on this alloy was all Type 3, which is essentially a thin, multilayer scale containing thickened areas of chromium sulfide. The scale morphology after 2101 hours was observed to contain areas of both Types 2 and 3 scale, together with about 10 percent of Type 1. In contrast, the thin scales formed on the 2 percent yttria-containing alloy, prepared by powder metallurgy, were solely Type 0 after 474 and 2101 hours of exposure.

The weight gains of the alloys based on the Fe-25Cr master alloy after isothermal exposure in the $H_2/H_2O/H_2S$ gas mixture at 700°C are illustrated in Fig. 10. Note that the weight gains for the Fe-25Cr, and the Fe-25Cr-20Ni master alloys increase monotonically with time, and that the additions that consistently result in reduced weight gains are silicon, hafnium, and yttrium. The relative effects of the additions are further illustrated, for 500 and 2000 hours exposure, in Fig. 11. Note that the largest, consistent effect was produced by 3 percent silicon, and that the maximum reduction in percentage relative weight change was only of the order of 65 percent. The poor performance of the 1 and 2 percent Al-containing alloys did not appear to be associated with any extensive, internal oxidation process but rather with a more rapid degradation of the scale to incorporate S-containing species.

Examples of the scale morphologies formed are shown in Fig. 12. The silicon-containing alloys formed essentially single-phase, thin, protective scales, although at 2107 hours the scale on the 3 percent silicon alloy is obviously multilayered. The scale on the 1 percent Al alloy shows signs of conversion to Type 2 morphology (which contains external protrusions of FeS) after 1104 hours exposure, while that on the 2 percent Al alloy contains approximately 20 percent of Type 2 morphology even after 164 hours of exposure. The scale formed on the 2 percent manganese-containing alloy was a thin, apparently single-phase, protective scale throughout the exposure period studied; nevertheless, this alloy consistently gave higher weight gains than the master alloy, since it consistently formed thicker scales.

The kinetic data for the Fe-25Cr-6Al-base alloys are difficult to interpret, because the scales formed on the alloys were thin, and small amounts of scale spallation resulted in large effects on the measured weight change. Weight change data as a function of exposure time for isothermal exposures at 700°C in the H₂/H₂O/H₂S gas mixture for these alloys are shown in Fig. 13; these data should be considered preliminary, since morphological examination of all the specimens has not yet been completed. For the cast alloys, note 0.1 percent yttrium and the 3 percent silicon additions appear to lead to extensive spallation. All of the alloys produced by powder metallurgy processing appear to undergo scale spallation, with the 2 percent silicon alloy being the worst offender. In fact, these preliminary data suggest that none of the additions act in a consistent way to improve the resistance to scale spallation of the Fe-25Cr-6Al master alloy.

Figures 14 through 16 show summaries of the information presented in the earlier figures for the effects of yttrium in its various forms, silicon, and niobium carbide on the weight change behavior of the alloys under the conditions studied so far. In these diagrams, the weight change measured for a given alloy is directly compared with the weight change for the pertinent master alloy exposed in the same test; data are again presented on the basis of 500-hour and 2000-hour exposures. For the case of yttrium metal added at the 0.1 and 1 percent level by conventional casting or by powder metallurgy processing, the greatest effect is exerted on the Fe-25Cr-20Ni base, and by the additions made by powder metallurgy as described earlier. The effect of such additions on the isothermal weight gains of the Fe-25Cr and Fe-25Cr-6Al master alloys are small or negligible. Silicon additions have a beneficial effect on the isothermal weight gain of the Fe-25Cr-20Ni alloy after 2000 hours exposure, with the effect increasing with increased silicon content from 1 to 3 percent by conventional casting and from 2 to 6 percent by powder metallurgy processing, while the powder-metallurgy produced additions are more effective than those produced by casting. Silicon additions also apparently decreased the weight gain of the Fe-25Cr and the Fe-25Cr-6Al master alloys, although the effect is not as large as on the Fe-25Cr-20Ni alloy. The effects of additions of niobium carbide and yttria are presented in Fig. 17 as

the effects of dispersoids, since both additions are present in the alloy base as discrete particles; note that the niobium carbide additions were only made to the Fe-25Cr-20Ni master alloy, while the yttria additions were made to the same master alloy and to the Fe-25Cr-6Al master. The niobium carbide dispersion added by rapid solidification processing was effective in reducing the weight gain after 500 and 2000 hours; the yttria dispersion added to the same master alloy by high-energy milling proved to be consistently more effective. The yttria additions made to the Fe-Cr-Al master alloy apparently did not reduce the tendency for scale spallation, and, in fact, after 2102 hours exposure, the yttria-containing alloy surprisingly showed greater weight loss than the unalloyed master.

Overall, the observed effects of the various alloying additions on the isothermal corrosion behavior at 700°C in the H₂/H₂O/H₂S gas mixture are as follows:

- For the Fe-25Cr master alloy, additions of yttrium, hafnium, and silicon reduce the weight gain, and apparently increase the time required for S-containing species to appear in the oxide scales. The effectiveness of these additions appears to increase with increasing level of the addition, for the two levels studied. Manganese appears to have a detrimental effect on the kinetics of this master alloy, although its effect does not appear to be to increase the rate at which the protective oxide scale breaks down to form sulfides; instead, the scales on this alloy have the form of thin, uniform, protective scales, but with additional mounds of loosely-attached Mn-containing corrosion product which may contain sulfide. Additions of Al at the 1 and 2 percent level to this alloy proved detrimental to the weight gain, but internal oxidation did not appear to be a major factor.
- For the Fe-25Cr-20Ni master alloy, additions of yttrium, hafnium, and silicon were not very effective when added by the conventional casting route; if there were any beneficial effect, it was not obvious with short-term exposures, but after long times the weight gains of these alloys were typically somewhat less than that for the master alloy. Additions of yttrium and silicon were quite effective when added by the rapid solidification powder metallurgy route and by the high-energy milling route; their effects appeared to be to delay the breakdown of the scale and incorporation of the sulfide species. Yttrium additions were more effective when made by high-energy milling than by rapid solidification than by conventional casting. The effectiveness of silicon added by rapid solidification was essentially the same whether added at the 2 percent or 6 percent level. Niobium added by the conventional casting route, Al, and Mn were detrimental at the levels used here. Niobium added by rapid solidification processing proved to be very effective in reducing the weight gain of this master alloy.

- For the Fe-25Cr-6Al master alloy, the preliminary results suggest that none of the additions exerted a very large effect on the weight gains of this master alloy. The higher levels of silicon additions, and yttrium added by rapid solidification and by high-energy milling were the most effective additions studied.

Table 1. XPS Data From H₂/H₂O/H₂S Exposures
(glovebox --> sealed cell --> XPS)

<u>Time, h</u>	<u>Fe</u>	<u>Cr</u>	<u>Ni</u>	<u>Al</u>	<u>Si</u>	<u>O</u>	<u>S</u>	<u>C</u>	<u>Comments</u>
<u>Fe-25Cr</u>									
0.25	2.9	22	-	2.1	2.5	59	1.1	9.8	
24	0.6	25	-	1.7	2.4	65	-	4.9	
96	-	26	-	-	5.2	67	-	2.2	
<u>Fe-25Cr-20Ni</u>									
0.25	8.8	14	-	2.8	3.3	58	0.9	12	
24	10	12	2.4	-	2.4	57	4.1	12	spalled area
24	10	3.0	4.3	3.8	3.6	34	13	22	non-spalled
96	13	14	tr	-	-	64	1.8	6	
<u>Fe-25Cr-6Al</u>									
0.25	6.1	10	-	7.2	4.4	57	0.4	15	
24	3.6	-	-	26	3.7	63	tr	3.3	
96	2.5	2.5	-	34	7.9	57	2.9	3.9	

Table 2. TEM Data From 0.25h H₂/H₂O/H₂S Exposures

STRUCTURE	COMPOSITION						COMMENTS
	Fe	Cr	Ni	Al	Mn	S	
<u>Fe-25Cr</u>							
Hexagonal (Cr, Fe) ₂ O ₃	8.7	90.1	-	-	0.8	0.4	grain size <1000 Å; thicker on gb's patches high in Fe, or Al
<u>Fe-25Cr-20Ni</u>							
50% hexagonal (Cr, Fe) ₂ O ₃ 50% spinel (Fe, Cr, Ni) ₃ O ₄	23.7	73.7	2.1	-	0.8	0.2	grain size <500 Å; thicker patches high in Fe, or Al
<u>Fe-25Cr-6Al</u>							
0.25 h: Spinel (Fe, Cr, Al) ₃ O ₄	54.9	29.6	-	13.9	0.5	1.0	grain size <300 Å; thicker areas high in Fe, or Cr, or Al
96 h: α-Al ₂ O ₃ Spinel (Fe, Cr, Al) ₃ O ₄	17.6	33.4	-	47.2	0.9	0.8	grain size <1000Å; thicker areas high in Cr (60-74%), above or below surface?

Figure 1. TEM Micrograph of Scale Formed on Fe-25Cr After 15 min. Exposure at 700°C to H₂/H₂O/H₂S Gas Mixture.

Figure 2. TEM Micrograph of Scale Formed on Fe-25Cr-20Ni Alloy After 15 min. Exposure at 700°C to $H_2/H_2O/H_2S$ Gas Mixture

Figure 3. TEM Micrograph of Scale Formed on Fe-25Cr-6Al Alloy After 15 min. Exposure at 700°C to H₂/H₂O/H₂S Gas Mixture

Figure 4. TEM Micrograph of Scale on Fe-25Cr-6Al Alloy After Exposure For 95 h at 700°C to $H_2/H_2O/H_2S$ Gas Mixture

Figure 5. Oxidation Kinetics at 700°C For Cast Fe-25Cr-20Ni, Isothermal, H₂/H₂O/H₂S

Figure 6. Weight Gain Data for Cast Fe-25Cr-20Ni-Based Alloys At 700°C, Isothermal Exposures in H₂/H₂O/H₂S With P_{O₂} = 10⁻²⁰ atm, P_{S₂} = 10⁻⁸ atm.

Figure 7. Weight Gain Data For Power Metallurgically-Produced Fe-25Cr-20Ni-Based Alloys at 700°C, Isothermal Exposures in H₂/H₂O/H₂S with P_{O₂} = 10⁻²⁰ atm, P_{S₂} = 10⁻⁸ atm.

Fe-Cr-Ni Alloys

* Indicates PM Alloys

Figure 8. Relative Effectiveness of Additions to The Fe-25Cr-20Ni Base.

Figure 9. Semi-Quantitative Comparisons of the Scale Morphologies Formed on Fe-25Cr-20Ni-Base Alloys

Figure 10. Weight Gains for Fe-25Cr-Based Alloys, Exposed Isothermally at 700°C in H₂/H₂O/H₂S Where P_{O₂} = 10⁻²⁰ atm, P_{S₂} = 10⁻⁸ atm.

Figure 11. Relative Effectiveness of Additions To The Fe-25Cr Base.

Figure 12. Semi-Quantitative Comparisons of the Morphologies of Scales Formed on Fe-25Cr-Base Alloys.

Figure 13. Weight Gains for Fe-25Cr-6Al-Based Alloys Exposed Isothermally at 700°C in H₂/H₂O/H₂S Where $P_{O_2} = 10^{-20}$ atm, $P_{S_2} = 10^{-8}$ atm.

Fe-Cr-Al Alloys

* Indicates PM Alloys

Figure 14. Relative Effectiveness of Additions To Fe-25Cr-6Al Base.

* Indicates PM Alloys

* Indicates PM Alloys

Figure 15. Effects of Y in Fe-25Cr-Base Alloys After 500 and 2000 h at 700°C in H₂/H₂O/H₂S.

* Indicates PM Alloys

* Indicates PM Alloys

Figure 16. Effects of Si in Fe-25Cr-Pase Alloys After 500 and 2000 h at 700 °C in H₂/H₂O/H₂S.

* Indicates PM Alloy

Figure 17. Effects of Dispersions on Fe-25Cr-20Ni and Fe-25Cr-6Al-Base Alloys After 500 and 2000 h at 700°C in H₂/H₂O/H₂S.

CWR-3 - INVESTIGATION OF THE EFFECTS OF MICROALLOY CONSTITUENTS,
SURFACE TREATMENT, AND OXIDATION CONDITIONS ON THE DEVELOPMENT
AND BREAKDOWN OF PROTECTIVE OXIDE SCALES

K. Vedula

Department of Materials Science and Engineering
Case Western Reserve University
Cleveland, Ohio 44106

INTRODUCTION

The focus of the current program is to obtain a better understanding of material behavior in fossil energy environments. The particular emphasis is on the protectiveness of oxide scales formed in atmospheres containing high pS_2/pO_2 ratios. Iron based alloys including Fe-25wt%Cr and Fe-25wt%Cr-20wt%Ni (which are Cr_2O_3 formers) and Fe-25wt%Cr-6wt%Al (which is an Al_2O_3 former) are base alloys for this investigation. Of particular interest are the effects of reactive element additions through bulk alloying as well as through ion implantation and the effects of surface modification through preoxidation.

DISCUSSION OF CURRENT RESULTS

In the previous semi-annual report a general comparison was made of the three groups of alloys exposed to severe conditions of $pS_2=10^{-9}$ and $pO_2=10^{-23}$ atmospheres at 700°C for 20 hours using gas mixtures of $H_2/H_2O/H_2S/Ar$. Of these alloys, the Fe-25Cr-20Ni alloys were the worst and the Fe-25Cr-6Al alloys were the best. The Fe-25Cr-20Ni alloys developed several microns of non-protective scale containing Fe and Ni sulfides along with Fe and Ni oxides near the surface. The behavior of the Fe-25Cr alloys suggested that the degradation of the initially formed Cr rich oxide scale started by enrichment of S leading to the formation of small sulfur-rich nodules. This was followed by iron enrichment through these nodules, and rapid oxidation of the iron to form larger nodules. The Fe-25Cr-Al alloy formed a protective layer of $\gamma-Al_2O_3$

which covered the entire surface. Eventually even this scale was penetrated by sulfur, resulting in the formation of sulfur-containing nodules. In these alloys, the additions of 1 wt% reactive elements, Y, Hf, La and Ce did not demonstrate any significant differences in the behavior. One of the problems, however, with these cast alloys was the segregation of the reactive elements.

An understanding of the evolution of the scales was further undertaken by using selected oxidizing conditions. Results of the detailed study for the base alloys and for some alloys containing reactive elements are presented below. In addition, preliminary results are presented for specimens which were preoxidized prior to the exposure to mixed gas atmospheres. Since the results obtained so far were for very severe atmospheres, which are selected in order to understand basic mechanisms, further experiments are being devoted to milder and more realistic atmospheres.

Part I. Evolution of Scales on Base Alloys

A detailed understanding of the basic mechanisms of degradation of the scales was undertaken by using selected oxidizing conditions (Table I), particularly at short times of exposures.

A. Fe-25Cr

The Fe-25Cr alloy was examined in more detail by comparing the nature of initial scale formed in an atmosphere containing no sulfur ($p_{O_2}=10^{-23.6}$) with that formed in a mixed gas environment ($p_{O_2}=10^{-23.6}$ and $p_{S_2}=10^{-7.9}$).

The scale formed on the Fe-25Cr alloy exposed for 30 mins to $p_{O_2}=10^{-23.6}$ atm. at 700°C was examined and found to be essentially pure Cr_2O_3 with a grain size of about 100 to 500 Å. When the same alloy was exposed to a mixed environment containing $p_{S_2}=10^{-7.9}$ and $p_{O_2}=10^{-23.6}$ atm. at 700°C for 15 and 30 mins., several precipitates are observed within the oxide scale. TEM/EDS analysis of the scale along with the TEM micrographs are presented in Figure 1 for these specimens. EDS and electron diffraction show that the background scale is almost pure Cr_2O_3 at 15

minutes and that this scale becomes richer in iron at 30 mins. The precipitates are rich in Cr and S at 15 minutes and contain significant amounts of Fe at 30 mins. Electron diffraction patterns of the scale confirm the Cr_2O_3 structure with precipitates of chromium sulfide ($\text{CrS}_{1.17}$).

Of particular significance is that in addition to the micron size sulfur-rich precipitates identified in the thin foils such as those illustrated in Figure 1, several very fine sub-micron size precipitates of $\text{CrS}_{1.17}$ were also identified as a dispersion in the background chromia scale. The larger precipitates are believed to have formed from the nuclei on the bare alloy surface, whereas the smaller ones must have formed due to local conditions within the oxide scale.

Multiplex scanning using auger spectroscopy of the background and of selected nodules on the scale (Figures 2a and 2b) show that the background scale contains a significant amount of Fe and S and that the stoichiometry of the Cr and O do not correspond to Cr_2O_3 . In order to check whether the measurement technique played a role in this observed deviation from stoichiometry, a pure Cr_2O_3 scale formed on the same alloy in pure oxygen at 900°C was examined in a similar manner and was shown to have a composition very close to the expected stoichiometry (Figure 2c). The chromium oxide background scale formed in the mixed gas environment is, therefore, significantly different from the Cr_2O_3 which forms in an oxygen environment. It contains significant amounts of Fe and S and the amount of Cr is well below that required for the Cr_2O_3 composition.

The nodules which form on this background contain some Cr and oxygen with substantial amounts of Fe and S compared with the background scale. Since the spot size for the auger analysis is about 1000 Å, these results suggest that the nodules are a very fine two-phase mixture of sulfide and oxide.

Depth profiling provides further insights, as shown in Figure 3, for a specimen exposed for 15 mins. and analyzed for the background, for a small nodule and for a larger nodule. Clearly the background at this location contains only a little Fe or S. The sulfur level in the background scale is, however, significant enough and the discrete nature of the distribution suggests that the sulfur is in the form of very fine

precipitates within the oxide and is consistent with the sub-micron size sulfides observed by transmission electron microscopy. The chromia scale, which is about 400 Å thick, has resulted in the Cr depletion in the alloy adjacent to the interface. The small nodule, which is not much thicker than the scale, contains a substantial amount of S and a small amount of Fe. The analysis of the larger nodule shows that the nodule has a much larger amount of S near its surface and also a larger amount of Fe than the smaller nodule. The simultaneous increase of Fe as well as S in the nodule suggests that in order for the nodule to become large, sulfur from the atmosphere and Fe from the alloy are essential. The combination of these with the Cr_2O_3 scale results in either a two-phase mixture of oxide and sulfide or a single phase oxy-sulfide. Of particular significance is the penetration of S as well as O towards the alloy/scale interface and the transport of Fe towards the gas/scale interface.

The characteristics of the scales described above suggest that some chromium sulfides nucleate on the bare metal surface along with chromium oxide and continue to grow in these conditions, whereas other fine sulfide precipitates may form within the oxide and present a path for further transport of sulfur through the oxide scale. The sulfides provide a rapid path for iron to diffuse out through the scale, resulting in the growth of nodules which appear to be two phase mixtures of oxides and sulfides. These nodules lead to the eventual breakdown of the scale.

B. Fe-25Cr-6Al

Since the degradation of the Fe-25Cr-6Al alloy requires longer times or more severe environments than the Fe-25Cr alloy, it was further investigated over a range of conditions which include $\text{pH}_2\text{O}/\text{pH}_2\text{S}$ ratios from 0.2 to 30 (Table I) and exposure times from 15 mins to 40 hours.

Nodule formation is observed on the surface of this Fe-25Cr-6Al alloy just as in the case of the Fe-25Cr alloy, but the severity of the nodule formation is much less in the alumina forming alloy. The severity of nodule formation, nevertheless, increases with time of exposure. A comparison of the scanning electron micrographs of the surfaces exposed for 1 hr and 20 hrs at $\text{pO}_2=10^{-23.6}$ and $\text{pS}_2=10^{-7.9}$ (Figure 4) shows that

the number of nodules as well as the size of the nodules increase with time of exposure. Alloy grains with different orientations reveal nodule formation of differing severity. In general, there appear to be three levels of perturbations on the scale surface. A small number of large nodules (several microns in size) are seen periodically; a large number of smaller nodules (0.1 to 0.5 μm) are distributed uniformly throughout the scale and, in addition, the background scale shows tiny bumps (about 0.1 μm) which may be the beginning of nodule formation. The large and the medium sized nodules increase in size (but not significantly in number) with increasing time of exposure.

Transmission electron microscopy shows that at very short times of 15 mins. at $p\text{O}_2=10^{-23.6}$ and $p\text{S}_2=10^{-7.9}$, the scale is essentially an oxide scale (Figure 5). The oxide is a mixture of Cr_2O_3 and Al_2O_3 with a very fine grain size. The electron diffraction as well as EDS analysis suggest that second phases are present in very small amounts within this oxide scale.

Transmission electron micrographs of the specimens oxidized for 1 hr and 20 hrs at $p\text{O}_2=10^{-23.6}$ and $p\text{S}_2=10^{-7.9}$ are shown in Figure 6. The darker precipitates in these micrographs are believed to be the medium sized nodules. The nodules which are observed were found to be predominantly rich in Cr and S with small amounts of Fe.

Of particular significance is the observation that TEM/EDS analysis of the background shows the scale changes from Cr rich oxide scale to Al rich oxide scale with longer exposure times (Table II). This means that the outer Cr_2O_3 scale is transformed to a $\gamma\text{-Al}_2\text{O}_3$ underneath it. Auger spectroscopy of the background scale confirms that Cr is enriched near the gas-scale interface and decreases towards the scale/alloy interface.

Depth profiling by scanning auger spectroscopy of a specimen exposed for 20 hrs to $p\text{O}_2=10^{-23.6}$ and $p\text{S}_2=10^{-7.9}$ (Figure 7) shows that the thin Al_2O_3 background scale is about 700 Å thick with a small amount of Cr enrichment near the surface and very little S. The small nodule, which is about 1200 Å in size contains significant amounts of S and Fe in it whereas the large nodule contains larger amounts of S and Fe. The O and S are transported far into the alloy beyond the scale/alloy interface

for the larger nodules suggesting a penetration of O and S into the alloy either as oxide/sulfide protrusions or as internal oxides and sulfides.

The nodule formation in the Fe-25Cr-6Al alloy is, therefore, similar to that in the Fe-25Cr alloys but is much slower, e.g. the 15 minute specimen for Fe-Cr alloy is similar to the 20 hr specimen for Fe-Cr-Al alloy. The nodules are Cr-rich oxide-sulfide mixtures near the gas/scale interface and contain significant amounts of Fe along with Cr near the scale/alloy interface.

The characteristics of the scales observed on the Fe-25Cr-6Al alloy, hence, suggest that the γ - Al_2O_3 scale forms very rapidly during the initial stages, presumably due to faster nucleation than a Cr_2O_3 scale and, hence, no significant sulfide precipitation is observed on the bare metal surface. With increased exposure, nodules containing sulfur form at a slow rate. The presence of the Al_2O_3 scale appears to hinder the transport of the alloying elements required for rapid sulfide formation.

C. Fe-25Cr-20Ni

This alloy was the most severely attacked in the experiments carried out for general comparison, as illustrated earlier. Short-term experiments were conducted in order to understand the evolution of this scale.

Specimens of this alloy, when oxidized in a p_{O_2} of $10^{-23.1}$ atm. for 15 mins., were found to be covered by almost pure Cr_2O_3 scale (Table III). Even during the heat up of the specimen in H_2 gas, before introducing the mixed gas environment, the scale formed was predominantly Cr_2O_3 .

However, as soon as the p_{S_2} of $10^{-7.9}$ atm. was included in the atmosphere for 15 min., the background oxide scale was found to become enriched in iron suggesting the formation of a spinel phase or Cr_2O_3 containing Fe. A large number of S rich nodules were also observed in the scale. Ni and S were observed to a small extent in the background scale, but in larger amounts in the nodules.

The specimen exposed for 30 minutes to the same mixed gas environment showed severe scale formation (Figure 8), although the severity was not uniform throughout the surface. In thicker portions of the

scale Cr rich sulfides (or oxy-sulfides) were detected, whereas in thinner regions, the scales were Cr_2O_3 and some spinel.

The rapid degradation of the Fe-25Cr-20Ni alloy under these conditions makes it more difficult to isolate the characteristics of the scale which may provide some insights into the growth mechanism. It is only possible to speculate that the reasons for the rapid deterioration of the scales may lie either in the much lower flux of Cr to the surface (since this is an FCC alloy compared with the BCC Fe-25Cr alloy) or in the formation of low melting sulfides containing Ni.

Part II. Effects of Bulk Reactive Element Additions

A. Fe-25Cr-6Al-1Y

Specimens of Fe-25Cr-6Al-1Y were exposed to the same environments as the base alloy and the SEM microstructures of resulting scales are shown in Figure 9 for scales formed after 1 hour and 20 hours at 700°C ($p_{\text{S}_2}=10^{-7.9}$ and $p_{\text{O}_2}=10^{-23.6}$ atm.). These figures show severe oxidation in the regions which were segregated with Y. These regions in the alloy have been shown by TEM to contain mostly Fe and Y in the form of an inter-metallic compound. The rapid oxidation of these regions is because of the low levels of Cr and Al. The matrix grains of these alloys show very little degradation compared with the base Fe-25Cr-6Al alloy (Figure 4), suggesting that the small amounts of Y dissolved in the matrix may be sufficient to play a beneficial role at least in this alloy.

B. Fe-25Cr-20Ni-1La

The analysis of this alloy also presented problems because of the regions which segregated with La during the casting process. However, the alloy containing La, when exposed to the same conditions as the base Fe-25Cr-20Ni alloy, showed more severe corrosion compared with the base alloy. TEM/EDS analysis of the scale showed that the preoxidized scale on this alloy contains very large amounts of Fe compared with the scale on the base alloy which is predominantly Cr_2O_3 (Table III). Even when exposed to the mixed gas for 15 mins., the alloy containing La showed

the scale as mainly iron-rich with significant amounts of S and very little Cr. These results suggest that La addition does not benefit this alloy in mixed gas environments. On the other hand, it appears to make the alloy corrode more severely.

Part III. Effect of Preoxidation Prior to Mixed Gas Exposure

A. Fe-25Cr-6Al

The Fe-25Cr-6Al alloy was preoxidized at 700°C for 1 hour using H₂ gas saturated with H₂O at room temperature ($p_{O_2}=1.9 \times 10^{-24}$ atm). SEM/TEM analysis of the resulting scale showed the background oxide scale to be a mixture of Al₂O₃ and Cr₂O₃ containing some sub-micron sized nodules of the spinel phase, FeCr₂O₄ (Figure 10a illustrates this scale). It is interesting that the aluminum content in the background oxide scale was less than the Al content in the background oxide scale formed in the earlier experiments in mixed gas at the same temperature.

When this pre-oxidized alloy specimen is exposed to a H₂/H₂O/H₂S/Ar atmosphere with $p_{O_2}=2.8 \times 10^{-24}$ and $p_{S_2}=1.2 \times 10^{-8}$ atm for 1 hour at 700°C, the FeCr₂O₄ nodules formed during the preoxidation developed into bigger nodules containing a significant amount of sulfur, since this phase provides an easy path for sulfur penetration. Another interesting observation is that the Al/Cr ratio in the background scale increased during the mixed gas exposure. Figure 10b illustrates the surface of the scale after the mixed gas exposure. Smaller nodules are also formed within the background oxide scale and may be the beginning of degradation of the background scale as well.

B. Fe-25Cr-20Ni

The Fe-25Cr-20Ni alloy was preoxidized at 700°C for 1 hour in an atmosphere of H₂/H₂O ($p_{O_2}=7.8 \times 10^{-24}$ atm). The oxide formed was predominantly Cr₂O₃, but did not cover the whole alloy surface even after one hour.

The preoxidized alloy specimen was exposed to a H₂/H₂S/H₂O/Ar atmosphere ($p_{O_2}=2.8 \times 10^{-24}$, $p_{S_2}=1.2 \times 10^{-8}$ atm) for 1 hour at 700°C.

During this exposure, the scale grew non-uniformly and was quite severely damaged. The thinner regions contained a mixture of iron-rich cubic and rhombohedral oxides. Within this oxide scale platelet-shaped precipitates of Cr-rich sulfide and rounder precipitates of Fe-rich sulfides were identified. The thicker regions showed a network of Fe-rich rhombohedral oxide between which large iron-rich sulfides were formed. This thicker scale appears to have formed on the surface of the alloy which was not properly covered during the preoxidation. The thinner part of the scale appears to show the beginning of degradation in the form of sulfide precipitates within the oxide scale which is becoming enriched in iron. Figure 11 illustrates the TEM micrographs of the two regions of the scale after the mixed gas exposure.

Research in Progress

The effects of preoxidation on subsequent degradation of the scales is being investigated in detail. Oxides preformed at 700°C do not appear to be very protective. Higher temperatures of preoxidation are being used to obtain more protective scales.

Scale formation and breakdown is being investigated for less severe conditions (higher values of pO_2). The less severe attack will allow us to isolate the early stages of degradation in more detail.

Several samples which were ion implanted with Y have been exposed to mixed gas atmospheres and are being examined.

Summary

The progress during this reporting period includes a detailed characterization of the evolution of the scales on base alloys exposed to severe mixed gas environments; an evaluation of the effects of reactive elements in the bulk form for two alloys; and a preliminary evaluation of the effects of preoxidation at 700°C on the subsequent breakdown of the scales in mixed gas environments.

TABLE I.
DETAILS OF THE CASES USED FOR THE EXPERIMENTS
Part I. Evolution of Scales

p_{H_2O}/p_{H_2S}	$\log p_{O_2}$ (atm)	$\log p_{S_2}$ (atm)	H_2O	Amount of Flow H_2S (cc/min)	Ar	Flow Rate (cm/sec)
<u>A. Fe-25Cr</u>						
1.9	-23.6	-7.9	4.95	2.61	63	0.82
<u>B. Fe-25Cr-6Al</u>						
0.2	-25.5	-7.9	0.71	3.55	22	0.83
1.0	-24.1	-7.9	3.14	3.14	40	0.80
1.9	-23.6	-7.9	4.95	2.61	63	0.82
6.0	-22.6	-7.9	9.03	1.51	115	0.82
8.0	-22.3	-7.9	9.97	1.25	127	0.81
30.0	-21.2	-7.9	34.55	1.16	141	0.80
<u>C. Fe-25Cr-20Ni</u>						
2.99	-23.15	-7.86	6.57	2.0	90	0.85

TABLE II.
Al/Cr RATIO IN BACKGROUND OF SCALES ON Fe-25Cr-6Al OXIDIZED IN
 $pO_2=10^{-23.6}$ ATM., $pS_2=10^{-7.9}$ ATM. AT 700°C, BASED ON TEM/EDS ANALYSIS

Exposure Time	15 mins.	30 mins	1 hr	5 hrs	10 hrs	20 hrs
Al/Cr Ratio	1.5	2.1	2.3	2.9	5.9	6.2

TABLE III
TEM/EDS RESULTS FOR Fe-25Cr-20Ni ALLOY SCALES

			Fe	Cr (at%)	Ni	
(A)	Fe-25Cr-20Ni Alloy exposed to heat-up and cool down cycle	area 1:	5.56	94.42		
		area 2:	8.61	91.31		
(B)	Fe-25Cr-20Ni Alloy exposed to $pO_2=10^{-23.1}$ atm for 15 mins. at 700°C	area 1:	3.35	96.12	0.53	
		area 2:	2.86	96.57	0.57	
(C)	Fe-25Cr-20Ni Alloys exposed to $pO_2=10^{-23.1}$, $pS_2=10^{-7.9}$ atm. for 15 mins. at 700°C	area 1:	Fe 22.59	Cr 61.51	Ni 2.11	S 1.74 (Background)
		area 2:	28.69	30.97	4.38	16.73 (precipitate)
			Fe	Cr	Ni	
(D)	Fe-25Cr-20Ni-1La exposed to $pO_2=10^{-23.1}$ atm for 15 mins at 700°C	area 1:	Fe 36.7	Cr 54.4	Ni 5.0	La 1.8
		area 2:	40.4	46.4	5.4	4.4
(E)	Fe-25Cr-20Ni-1La exposed to $pO_2=10^{-23.1}$ $pS_2=10^{-7.9}$ for 15 mins at 700°C	area 1:	68.0	9.3	9.3	--
		area 2:	79.7	8.0	4.5	1.6
						6.2
						1.9

[illegible]

Mass spectrum of the sample showing relative intensity versus m/z . The base peak is at m/z 43. Other significant peaks are labeled at m/z 39, 55, 67, 77, 91, and 105.

Figure 1. Transmission electron micrographs and EDS analysis of the scales formed on Fe-25Cr exposed to $pO_2=10^{-23.6}$, $pS_2=10^{-7.9}$ atm. at 700°C for (a) 15 mins and (b) 30 mins.

(a)

	Cr	O	Fe	S
Region 1	30.32	63.69	3.70	2.28
Region 2	29.97	61.80	4.60	3.63

(b)

	Cr	O	Fe	S
Region 1	28.47	59.20	4.98	7.35
Region 2	25.37	47.36	15.89	11.38
Region 3	19.74	51.42	18.98	9.86

(c)

	Cr	O
Region 1	40.66	59.34
Region 2	41.40	58.60
Region 3	39.29	60.71

Figure 2. Comparison of multiplex analysis of initial scales formed on the surface of Fe-25Cr alloy exposed to $pO_2=10^{-23.6}$, $pS_2=10^{-7.9}$ atm. at 700°C for (a) 15 mins. and (b) 30 min with (c) a Cr_2O_3 scale formed on the same alloy in oxygen at 900°C.

(a) SEM Micrograph

(b) Background 3

(c) Small Nodule 4

(d) Large Nodule 1

Figure 3. Depth profile analysis using scanning auger spectroscopy of selected regions on the surface of Fe-25Cr exposed to $p_{O_2}=10^{-23.6}$, $p_{S_2}=10^{-7.9}$ atm. at 700°C for 15 minutes.

Figure 4. Fe-25Cr-6Al exposed to $p_{O_2}=10^{-23.6}$, $p_{S_2}=10^{-7.9}$ atm. at 700°C. (a) for 1 hr and (b) for 20 hrs.

Figure 5. Transmission electron micrograph of the scale formed on Fe-25Cr-6Al exposed to $p_{O_2}=10^{-23.6}$, $p_{S_2}=10^{-7.9}$ atm. at 700°C for 15 mins.

(a) TEM Micrograph

EDS Analysis of Background

EDS Analysis of Precipitate

(b) TEM Micrograph

EDS Analysis of Background

EDS Analysis of Precipitate

Figure 6. Transmission electron micrographs of the scales formed on Fe-25Cr-6Al exposed to $p_{O_2}=10^{-23.6}$, $p_{S_2}=10^{-7.9}$ atm. at 700°C for (a) 1 hr and (b) 20 hrs.

(a) SEM Micrograph

(b) Background 3

(c) Small Nodule 4

(d) Large Nodule 1

Figure 7. Depth profile analysis using scanning auger microscopy of selected regions on the surface of Fe-25Cr-6Al alloy exposed to $p_{O_2}=10^{-23.6}$, $p_{S_2}=10^{-7.9}$ atm. at 700°C for 20 hrs.

Figure 8. Scanning electron micrograph of Fe-25Cr-20Ni alloys exposed to $pO_2=10^{-23.1}$, $pS_2=10^{-7.9}$, 700°C, for 30 mins.

Figure 9. Fe-25Cr-6Al-1Y exposed to $pO_2=10^{-23.6}$, $pS_2=10^{-7.9}$ atm. at 700°C (a, for 1 hr and (b) for 20 hrs.

Figure 10. Fe-25Cr-6Al (a) preoxidized at 700°C for 1 hr in $pO_2=1.9 \times 10^{-24}$ atm. (b) preoxidized and exposed to $pO_2=2.8 \times 10^{-4}$, $pS_2=1.2 \times 10^{-8}$ at 700°C for 1 hr.

Figure 11. TEM microstructure of Fe-25Cr-20Ni alloy preoxidized at 700°C for 1 hr in $pO_2=8.2 \times 10^{-25}$ and exposed to $pS_2=1.2 \times 10^{-8}$ and $pO_2=2.8 \times 10^{-24}$ for 1 hr at 700°C.

LBL-3 - STUDIES OF MATERIALS EROSION IN
COAL CONVERSION AND UTILIZATION SYSTEMS

A. Levy

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

INTRODUCTION

The erosion of material surfaces by small solid particles carried in gas and liquid carriers is being investigated. The materials are tested over a range of conditions that simulate portions of the operating environment of containment surfaces in coal gasification, liquefaction and fluidized bed combustion processes. The effects of material's properties, microstructures and compositions on their erosion behavior are determined. The effects of elevated temperature corrosion in combination with the erosion are studied to determine the mechanisms and rates of the combined surface degradation modes.

DISCUSSION OF CURRENT ACTIVITIES

Erosion-Corrosion Studies

Character and Erosivity of Particles

An investigation is underway to relate metal wastage of boiler heat exchanger alloys to the characteristics of the particles that impact the tubes in service. Bed material, sand and limestone from different operation cycles of several bubbling and circulating fluidized bed combustors (BFBC, CFBC's) are being tested in the study.

The bed materials from five pilot or production bubbling (BFBC) and circulating (CFBC) atmospheric fluidized bed combustor were characterized and used to erode 1018, plain carbon steel at 25° and 450°C at particle velocities of 10 and 20 m/s at impact angles of $\alpha = 30^\circ, 90^\circ$. The

different test bed material particles have been designated Nos. 1 - 7. Bed materials 1 and 2 are from the same CFBC but had different limestone contents in the charge material. Bed material No. 6 is from the same BFBC as No. 5 but had a different chlorine content coal fuel. A test time of 5 hours was used at two particle loadings, 375g (at $V = 20$ m/s) and 600g (at $V = 10$ m/s), which resulted in steady state material loss conditions, see Figure 1. Single composition erodents SiO_2 and SiC were also used to erode the 1018 steel at the same test conditions and their erosivities were compared to those of the bed materials.

Table 1 shows the microhardness of the two principal types of constituents in the bed materials. Table 2 shows the thickness loss of the specimens tested using erodent particles of the seven bed materials. The metal wastages in the specimens were determined by thickness changes of cross sections of samples using microscopic micrometer measurements. The lower microhardness of the SiO_2 in bed materials 5 and 7, from BFBC's, may be due to the fact that this SiO_2 is material that was not cleaned out of the coal fuel rather than the SiO_2 that was purposely added in the form of sand to the charges of the CFBC's of bed materials 1 - 4. The different basic source of the SiO_2 probably accounts for the two different hardness regimes seen in Table 1. Table 3 compares the erosivity of the particles from different locations in the CFBC's of bed material Nos. 2 and 4 as well as the erosivity of SiC and SiO_2 particles.

Figures 2 and 3 show the appearance and the EDX peak analyses of the bed material particles from different units. Figure 4 shows the appearance and the EDX peak analyses of sand and limestone from several units.

The constituents in the various bed materials varied considerably and, as a result, so did their erosivities. For instance, the higher SiO_2 content with its greater angularity and strength/hardness and lower CaO content made CFBC bed material No. 1 particles more erosive than bed material No. 4 particles (see Tables 1 and 2). For the same reason, higher SiO_2 content, angularity, and hardness made CFBC's bed material No. 3 particles more erosive than BFBC bed material Nos. 5 and 7 particles. The deliberate addition of sand as a stabilizing constituent in the CFBC's (bed material Nos. 1 - 4) made their bed material considerably

TABLE 1
MICROHARDNESS OF BED MATERIALS

BED MATERIAL	MICROHARDNESS (Hv100)	
	SiO ₂	CaO, CaCO ₃
No. 1 *	1232	112
No. 2 *	881	110
No. 3 *	1074	59
No. 4	878	98
No. 5 **	470	99
No. 7 88	777	99

* SiO₂ is majority

** CaO/CaCO₃ are majority

TABLE 2
SUMMARY OF THICKNESS LOSS OF 1018 STEEL

BED MATERIAL	No. 1	No.2	No.3	No. 4	No.5	No.6	No.7
Thickness loss (μ m)	7.9	6.6	4.8	5.4	3.2	2.3	3.1

TEST CONDITIONS

T = 450°C

α = 30°

V = 20 m/s

Loading 375 gm

Particle size 250 μ m

* Different specimen used for each data point

Figure 1. Incremental erosion rate curves for (a) $V = 10 \text{ m/s}$ and (b) $V = 20 \text{ m/s}$.

A dark, high-contrast, black and white photograph of a textured surface, possibly a book cover or endpaper. The image shows vertical lines and a rough, aged appearance, with some lighter areas suggesting wear or different materials. The overall tone is very dark, with the texture being the primary visual element.

XBB 886-6185 A

Figure 2. Appearance and the EDX peak analyses of the FBC bed material Nos. 1, 4.

Appearance of BFBC (Particle No.7)

Composition of Particle No.7

Appearance of CFBC Particle No.5

Composition of Particle No.5

Appearance of CFBC (Particle No.3)

Composition of Particle No.3

250µm AFBC Particles

Figure 3. The appearance and the EDX peak analyses of the FBC bed materials Nos. 3, 5 and 7.

TABLE 3
CFBC PARTICLE EROSIVITY

ERODENT		TEST CONDITIONS *		THICKNESS LOSS
Bed Material No.	Type	Particle Size (μm)	Temperature, $^{\circ}\text{C}$	(μm)
2	bed material	250	25	5.8
4	bed material	250	25	5.0
4	bed material	all sizes, ave. 300	25	5.5
2	bed material	250	450	6.6
2	sand	250	450	7.0
2	sand	all sizes, ave. 450	450	12.5
2	limestone	250	450	4.0
2	limestone	all sizes, ave. 800	450	5.8
2	precipitator ash	130	450	3.4
4	bed material	250	450	5.4
4	bed material	all sizes, ave. 300	450	5.8
4	sand	250	450	6.0
4	sand	all sizes, ave. 230	450	5.5
4	limestone	250	450	4.1
4	limestone	all sizes, ave. 300	450	4.5
LBL	SiC	250	450	16.3
LBL	SiO ₂	250	450	12.3

* TEST CONDITIONS

T = 5 hours

$\alpha = 30^{\circ}$

V = 20 m/s

Solids Loading 375 gm

1018 steel

more erosive than those from the BFBC's (bed material Nos. 5 - 7) which contained only residual SiO₂ that was not removed in the coal cleaning operation.

Table 3 indicated that bed materials from two different CFBC's had similar room temperature (25 $^{\circ}\text{C}$) erosion rates. At elevated test temperatures the sand used in the CFBC of bed material No. 2 was more erosive than that used in the CFBC of bed material No. 4. This was the reason for the higher elevated temperature erosivity of bed material No. 2. Limestone is less erosive than either sand or bed material. The more angular SiC and SiO₂ particles procured for earlier erosion investigations were more erosive than any of the bed materials. From

Figures 2 and 3 it can be seen that the bed material particles tend to be on the round side.

Comparing the data in Table 3 with the particle size/shape shown in Figure 4 it can be seen that the larger sand particles used in the CFBC of bed material No. 2 compared to those used in the CFBC of bed material No. 4 at similar hardnesses and angularity, also contributed to making the bed material No. 2 particles more erosive than bed material No. 4 particles. The highly angular limestone particles used in the CFBC of bed material No. 4 are much softer than sand and, therefore, are less erosive. Also, CaO in the bed material appears to promote the formation of a protective layer on the metal surface.

Bed Material Layer Effects

Figures 5 - 7 show the surface and cross section of the samples eroded-corroded by AFBC bed material Nos. 1, 4 and 5 particles. From Figure 5 it can be seen that a low CaO content in the bed material (less limestone was used in the CFBC of bed material No. 1) did not result in the formation of a protective layer of bed material. The scale that formed was consolidated and cracked and spalled. Craters in the thin scale in the upper micrograph of Figure 5 are similar to craters on the surface of the 25°C test specimens. This indicated that the scale was very thin and intermittent. The result was the highest thickness loss of all the erodents tested, see Table 2. Addition of limestone in the CFBC of bed material No. 2 reduced the thickness loss, compared to bed material No. 1.

Figure 6 from the CFBC of bed material No. 4, which utilized considerable limestone, indicated that a layer of protective bed material containing CaO developed on the surface. The resulting thickness loss was lower than the bed material No. 1 particles caused. High sulfur content in the bed material did not appear to be detrimental and may even have helped the formation of the protective scale. From Figure 7 it can be seen that a thick layer of segmented bed material formed on the surface that prevented iron oxide from forming. The resulting protection markedly reduced the thickness loss. Sulfur appears to

Appearance of Sand(in bed material No.1,2) 200µm

Composition of sand(in bed material No.1,2)

Appearance of sand(in bed material No.4) 200µm

Composition of sand(in bed material No.4)

Appearance of limestone(in bed material No.4) 200µm

Composition of limestone(in bed material No.4)

1013 Steel
 Nozzle Tester T=450°C
 Corrosion-Front c=30°
 Sand and Limestone Air
 t=5hr (175gm) V=20m/s

X88 8810-9721

Figure 4. The appearance and the EDX peak analyses of sand and limestone from different units.

Surface (T=450°C)

10 μm

Composition of surface

Cross section (T=450°C)

10 μm

Composition of cross section (Position 1)

Surface (T=25°C)

10 μm

Composition of surface

1018 Steel
 Mossle Tester T=25°C, 450°C
 Corrosion-Erosion α=30°
 250um CPBC Particle(Particle No.1) Air
 t=5hr (375gm) V=20m/s

XBB 887-7272 A

Figure 5. The surface, cross section and the EDX peak analyses of 1018 steel eroded-corroded by CFBC particles No. 1.

Composition of surface

Composition of cross section (Position 1)

Composition of cross section (position 2)

1018 Steel
 Nozzle Tester $t=450^{\circ}\text{C}$
 Corrosion-Erosion $\alpha=30^{\circ}$
 250µm CFBC (Particle No.4) Air
 $t=5\text{hr}$ (375gm) $V=20\text{m/s}$

XBB 887-7274 A

Figure 6. The surface, cross section and the EDX peak analyses of 1018 steel eroded-corroded by CFBC particles No. 4.

1018 Steel
 Mossie Tester T=450°C
 Corrosion-Erosion α=30°
 250μm BFBC (Particle No.5) Air
 t=5hr (375gm) V=20m/s

XBB 887-7275 A

Figure 7. The surface, cross section and the EDX peak analyses of 1018 steel eroded-corroded by BFBC particles No. 5.

have played the same role as it did in the bed material No. 4 deposit.

Effect of Cr and Si Content on Thickness Loss

Alternate low chromium content steels containing extra silicon were tested at 650°C and 450°C at $\alpha = 30^\circ$ and 90° , $V = 10$ m/s and 20 m/s using CFBC bed material No. 2. The tests were carried out in the LBL elevated temperature, nozzle type erosion tester. For comparison the low chromium content regular silicon containing steel and 9Cr1Mo steel were also tested. The typical compositions of the steels tested are listed in Table 4.

TABLE 4
TYPICAL ALLOY COMPOSITIONS (WT. %)

ALLOY	Fe	C	Cr	Mo	Mn	Si	S	P	other
2.25Cr1Mo	Bal	0.15	2.0 ~ 2.5	0.9 ~ 1.1	0.3 ~ 0.6	≤ 0.5	≤ 0.03	≤ 0.03	
2.5Cr0.55Mo1.4Si	Bal	0.1	2.5	0.55	0.45	1.4	< 0.02	< 0.03	
5Cr0.5Mo1.5Si	Bal	0.11	4.84	0.51	0.51	1.46	0.013	0.013	Cu 0.11
9Cr1Mo	Bal	0.15	8.0 - 10.0	0.9 - 1.0	0.45	0.5 - 1.0	0.03	0.03	

Table 5 is a summary of the test results on the alternate steels, compared with 2½Cr1Mo with regular silicon content steel and 9Cr1Mo steel. From Table 5 it can be seen that the addition of the extra silicon in tubing steels reduced the erosion-corrosion thickness loss at considerably lower particle velocities than were used in earlier studies of the effect of silicon content on E-C of Cr steels. The 2.5Cr0.55Mo1.4Si alloy had a very low, thickness loss, especially at 650°C, compared to other alloys and particularly compared to the standard 2.25Cr1Mo steel.

Figures 8 and 9 show the surface and cross section and the EDX peak analyses of 2.25Cr1Mo steel and 9Cr1Mo steel respectively tested at 450°C, $V = 20$ m/s, $\alpha = 30^\circ$ using 250µm CFBC bed material No. 2 particles. From these micrographs it can be seen that at 450°C 2.25Cr1Mo alloy had a similar thickness loss to 9Cr1Mo steel and essentially the same mixed bed material - iron oxide composition and morphology on its surface.

Surface

10µm

Composition of surface

Cross section

10 µm

Composition of cross section(position 1)

Composition of cross section(Position 2)

2.25Cr1Mo Steel
 Nozzle Tester T=450°C
 Corrosion-Erosion α=30°
 250µm CFBC Particle(Particle No.2)
 t=5hr(375gm) Air V=20m/s

Figure 8. The surface, cross section and the EDX peak analyses of 2.25Cr1Mo steel tested at T = 450°C.

Surface

10µm

Composition of surface

Cross section

10µm

Composition of cross section(position 1)

Composition of Cross section(position 2)

9Cr1Mo Steel
 Nossle Tester T=450°C
 Corrosion-Erosion α=30°
 250µm CFBC Particle(Particle No.2)
 t=5hr(375 gm) Air V=20m/s

Figure 9. The surface, cross section and the EDX peak analyses of 9Cr1Mo steel tested at T = 450°C.

TABLE 5
EROSION-CORROSION RATE

TEST CONDITIONS				THICKNESS LOSS (μm)			
T	V	α	Loading	2.25Cr1Mo	2.5Cr0.55Mo1.4Si	5Cr0.5Mo1.5Si	9Cr1Mo
650°C	20 m/s	30°	375 gm	53.3	20.0	29.0	37.5
650°C	20 m/s	90°	375 gm	19.48	7.95	12.25	17.38
450°C	20 m/s	30°	375 gm	5.53	3.33	5.30	5.13
650°	10 m/s	30°	600 gm	15.08	1.40	2.50	1.75

ERODENT PARTICLES: No. 2

Figure 10 shows the surface, cross section and EDX analysis of the 2.5Cr0.55Mo1.4Si steel tested at 450°C, $V = 20$ m/s, $\alpha = 30^\circ$ using 250 μm CFBC bed material No. 2 particles. It can be seen that at 450°C 2.5Cr0.55Mo1.4Si steel had a much thinner mixed bed material - iron oxide scale and a lower thickness loss than the regular Si content chromium containing steel, see Figure 8 and Table 5.

Figures 11 and 12 show the surface, cross section and the EDX analyses of 2.25Cr1Mo steel and 2.5Cr0.55Mo1.4Si steel, respectively, tested at $T = 650^\circ\text{C}$, $\alpha = 30^\circ$, $V = 20$ m/s. From Table 5 it can be seen that at 650°C, the thickness loss of the 2.5Cr0.55Mo1.4Si alloy was less than half that of the 2.25Cr1Mo alloy. Both alloys formed an iron oxide scale with a small amount of CaO in it. The remaining surface scale morphology of the two alloys appeared to be similar. However, the scale on the 2½Cr1Mo steel in Figure 11 had spalled off nearly to the scale-metal interface. This extensive spalling occurred both during the test and at cool down. The loss of scale during the test is what accounted for the thickness loss listed in Table 5. The scale cross section in Figure 12 was the condition of the scale during the test. There was no evidence of spalling either during the test or on cooldown on the 2.5Cr0.55Mo1.4Si steel, which accounted for the lower metal thickness loss.

At the lower, 10 m/s particle velocity, the improvement of the additional Si content alloy over the standard Si content alloy was remarkable. The additional silicon appears to have developed a more

Surface

10µm

Composition of surface

Cross section

10µm

Composition of Cross section(Position 2)

Composition of Cross section(position 1)

2.5Cr0.55Mn0.4Si Steel
 Nozzle Tester T=450°C
 Corrosion-Erosion $\alpha=30^\circ$
 250µm CPBC Particle(Particle No.2)
 $t=5hr(375gm)$ Air V=20m/s

Figure 10. The surface, cross section and EDX peak analyses of 2.5Cr0.55Mn0.4Si steel tested at T = 450°C.

Surface

10 μ m

Composition of Surface

Cross section

10 μ m

Composition of Cross section(Position A)

Composition of Cross section(Position B)

2.25Cr1Mo Steel
 Hossle Tester T=650°C
 Corrosion-Erosion $\alpha=30^\circ$
 250 μ m CPBC Particle (Particle No.2)
 t=5hr(375gm) Air V=20 m/s

Figure 11. The surface, cross section and the EDX peak analyses of 2.25Cr1Mo steel tested at T = 650°C.

Surface

10 μ m

Composition of Surface

Cross section

10 μ m

Composition of Cross section(Position A)

Composition of Cross section(Position B)

2.5Cr0.55Mn1.4Si Steel
 Nozzle Tester T=650°C
 Corrosion-Erosion $\alpha=30^\circ$
 250um CPBC Particle(Particle No.2)
 t=5hr(375gm) Air V=20 m/s

Figure 12. The surface, cross section and the EDX peak analyses of 2.5Cr0.55Mn1.4Si steel tested at T = 650°C.

protective combined iron oxide and bed material scale. The reasons for the marked difference in the behavior of the 2 alloys at 650°C are being determined.

NIST-3 - MECHANISMS OF GALLING AND ABRASIVE WEAR

L. K. Ives, M. B. Peterson, and E. P. Whitenton

Metallurgy Division
National Institute of Standards and Technology
Gaithersburg, MD 20899

INTRODUCTION

The successful commercial development of direct coal-fueled diesel engines depends on solving severe wear problems that are not encountered with present day oil-fueled engines. The purpose of this program is to develop a fundamental understanding of the processes and mechanisms that are responsible for wear at the critical piston ring / cylinder wall contact. Particulate matter both from the raw fuel and from combustion products enters the piston ring / cylinder wall contact region and causes rapid wear as a result of direct abrasion of the ring and cylinder wall materials and/or by interfering with the normal lubrication process. In this program, analyses and tests are carried out on raw fuel materials and combustion particulates to determine their abrasion characteristics. Laboratory wear tests are conducted under carefully controlled conditions that are consistent with those occurring at the piston ring / cylinder liner contact in the diesel engine. The effects of test conditions, different types of particulate materials, different lubricants and lubricant additives, and various specimen materials are studied.

DISCUSSION OF CURRENT ACTIVITIES

The investigation of wear mechanisms at the piston ring / cylinder liner contact of the coal-fired diesel

engine was begun at the initiation of this reporting period. Work was conducted in three different areas: 1) the acquisition and assessment of background information on wear in direct coal-fueled diesel engines; 2) the characterization of coal fuel and combustion particulates; and 3) laboratory wear testing. Progress in each of these areas will be summarized in the following paragraphs.

Background

The effort to develop a commercially viable, direct, coal-fueled diesel engine has a long history. Work was carried out in Germany dating almost from the time of the invention of the diesel engine by Rudolph Diesel in 1884 and continued to the end of World War II. This effort was largely unsuccessful. Among the major technical problems encountered were difficulties with injection of the coal dust fuel and extremely high wear rates, particularly of the injector nozzles, piston rings, and cylinder walls. The recent development of high quality, low ash, coal-water slurry fuels and the demonstration of their efficient combustion in medium and slow speed diesel engines has lead to renewed interest and current strong support in the development of commercial engines.

Despite the fact that modified diesel engines have been demonstrated to run on coal-slurry fuels, extremely high wear rates are still encountered. Cylinder liner and piston ring wear rates have been reported^{1,2} to range from about twenty to several hundred times that obtained when conventional No. 2 diesel fuel oil is used. The wear rate was found to increase with increasing concentration of ash in the coal. Complete removal of the mineral matter which is responsible for the ash is not, however, economically feasible. In addition, it is not entirely clear that wear

would not be high even in the absence of mineral contaminants. Clingenpeel et al.² point out in discussing their results that the wear rate vs. ash concentration curves do not extrapolate to oil-fired diesel values at zero ash concentration but are significantly higher.

The mechanisms responsible for increased piston ring and cylinder wall wear with coal-slurry fuel have not been the subject of a detailed analysis. In general, it has been assumed that the mechanism is one of abrasive wear caused by hard mineral and/or ash particles. Nydick et al.¹, however, observed topographic features that they considered to be the result of severe, metal-on-metal sliding wear due to an inadequate oil film. It was thought that the coal and ash particles might absorb or adsorb the oil film on the cylinder wall leaving it poorly lubricated.

Although abrasion by hard particulate contaminants is often cited as being a major source of wear at lubricated contacts, only a few studies have addressed this problem. A brief review of some aspects of the problem can be found in reference 3. Recently Mehan⁴ has reported on laboratory pin-on-disk wear tests that were designed to provide information on the selection of materials to resist wear in the coal-fired diesel. Most of his tests were conducted with Al_2O_3 as the abrading particles. Additive free mineral oil was used as a lubricant. His results indicated that by using tungsten carbide specimen materials the wear rate could be reduced to a level that would be acceptable in the diesel engine.

Wear at the piston ring / cylinder liner contact in the coal-fired diesel engine appears to be a combination of three-body/ abrasive wear and sliding wear under boundary lubrication conditions. A number of different processes

may be involved. The particles if sufficiently hard may remove material directly by an abrasion mechanism. Sliding wear may be enhanced as a result of the roughening of the surface by the abrasive particles. The abrasive particles may damage or remove a protective boundary lubrication film leading to a condition of scuffing or galling. Alternatively, disruption of a reactive boundary film may lead to enhanced chemical wear. Other factors which may have a significant influence on wear rate are particle hardness, friability, concentration, and size. Embedment of particles in one or both of the sliding surfaces may also affect wear. The wear process is complex and will require careful analysis and controlled testing if the critical factors and relationships are to be revealed.

Coal Fuel Particles

Samples of engine grade coal-water slurry materials were received from Otisca Industries and Amax for study. Only the Otisca Industries material has been examined in detail at this time. Typically, the Otisca fuel consists of 50 wt.% solids in water and 0.35 wt.% ash. The composition of the coal solids is given in Table 1. and of the ash in Table 2, according to information supplied by Otisca. The composition of coal from different lots and sources will of course vary from these values.

Table 1. Typical coal solids analysis, dry.

Carbon	82.96 wt. %
Hydrogen	5.34 wt. %
Nitrogen	2.08 wt. %
Chlorine	0.18 wt. %
Sulfur	0.70 wt. %
Ash	0.72 wt. %
Oxygen(diff.)	8.02 wt. %

Table 2. Typical ash analysis (parts per million).

Silica	661
Alumina	812
Titania	39
Ferric Oxide	986
Lime	406
Magnesia	101
Potassium Oxide	17
Sodium Oxide	16
Sulfur Trioxide	471
Phosphorus Oxide	35
Ignition loss	14
Undetermined	42

An SEM micrograph of coal particles from a slurry sample is shown in Fig. 1. The particles have a more-or-less equiaxed shape and are below the nominal maximum specified size of 10 μm . Representative energy dispersive x-ray spectra from two particles are shown in Fig. 2a and b. The spectra give a qualitative indication of the elements present with atomic numbers greater than Be. The large Cu peaks are from the substrate. This substrate material was chosen because Cu is not one of the elements that is present in the coal, and the characteristic peaks

Fig. 1. SEM micrograph of coal particles.

do not overlap peaks of most of the other elements of interest. The detectable elements from the particle analyzed in Fig. 2a were primarily C and small amounts of O and S. The particle analyzed in Fig. 2b contained in addition small amounts of Al and Si. Approximately 20 particles have been analyzed and none were found to be primarily mineral matter without carbon. Although more particles need to be examined, it appears that most of the mineral material is incorporated within the coal particles. This is important because it indicates that much of the hard, potentially abrasive, mineral content of the coal consists of small inclusions in the larger coal particles. In this form, the resulting abrasion would be far less severe than if the mineral content consisted of separate particles of the same size as the coal particles.

Combustion Particulates

C. Spiro of General Electric Corporation has carried out extensive analyses on combustion particulates from coal-fueled turbine engines⁵ as well as some studies on diesel particulates. Despite differences in combustion conditions, Spiro has found that the particles are similar⁶. He was able to provide for our investigation a few milligrams of diesel exhaust particulate from one of the test runs conducted at General Electric and several grams of turbine particulate. Although this program has no direct interest in turbine particulate, there was sufficient material available for use in laboratory wear tests. Unfortunately, this was not the case for diesel particulate. Because of the similarity of the two materials, it was considered that the turbine particulate might be used to give some indication of the wear behavior of diesel particulate.

Fig. 2a and b. Typical x-ray spectra from coal particles.

Figure 3 is an SEM micrograph of a representative sample of diesel exhaust particulate. Particles having several different morphologies are present. In general, they can be classified as being either spherical, porous, or blocky in character. The spherical particles were probably formed as a result of the condensation and subsequent solidification of a molten mass. The porous

Fig. 3. SEM micrograph of diesel exhaust particulate.

particles, on the other hand, very likely represent the partial combustion or volatilization of coal particles, while the blocky particles appear to be coal particles that were essentially unaffected by the combustion environment, i.e., were not burned.

Representative x-ray spectra from each of the different particle types are shown in Fig. 4 a-c. The spectrum in Fig. 4a, obtained from a spherical particle, indicates the presence of most of the principle elements contained in the ash analysis of Table 2. The spectrum in Fig. 4b from the porous particle also contains several of the principle elements of the ash analysis but, in addition, exhibits a large C peak, suggesting incomplete combustion. Also, sulfur is present at a rather high concentration, but was not detected in the spherical particle. Presumably, this is because complete combustion of a particle converts the sulfur to a gaseous product

Fig. 4. X-ray spectra from spherical diesel exhaust particles. a) Spherical particle. b) Porous particle. c) Blocky particle.

which leaves the system in that form or as a vapor. Finally, the spectrum in Fig. 4c from the blocky particle is nearly identical to that obtained from an unused coal particle shown in Fig. 2b. This tends to confirm the proposition that the particle passed through the engine without being affected by combustion.

A simple test was devised to obtain information on the abrasion characteristics of individual particles. The test is conducted as follows: Particles are dispersed onto a carefully polished substrate. A polished slider of the same material as the substrate is then pressed against the substrate and displaced by a distance amounting to a fraction of a millimeter. Some of the trapped particles are forced to slide or roll between the surfaces. If the particles have sufficient strength and hardness, indentations or grooves will be produced in the substrate and these can be observed in the SEM. Because of the relatively low concentration of particles employed and the small sliding distance, the particle responsible for the damage often remains in place where it can be characterized in relation to the damage caused.

Some preliminary results have been obtained with copper as the substrate. Figure 5a shows the groove produced by a diesel exhaust particle. The x-ray spectrum from the particle is shown in 5b. The similarity of the spectrum to that obtained from an unburned coal particle, Fig. 2b, suggests that this particle was relatively unaffected by the combustion process. The damage to the copper substrate is substantial, and the particle itself has apparently been crushed. Several other similar examples of damage to copper by exhaust particles were observed. Copper is relatively soft compared to most of the piston ring and cylinder liner materials that might be used in the diesel engine; however, it may not be soft

Fig. 5. a) Scratch in copper surface and associated diesel exhaust particle. b) X-ray spectrum from particle in a).

compared to some of the protective boundary lubrication films that are formed on the ring and liner surfaces of an operating diesel engine.

For comparison, a similar abrasion test was conducted on unburned coal particles. Figure 6 shows the scratch that was produced by a coal particle. In this case the particle appears to have suffered little damage itself.

In future experiments, substrates other than copper will be employed in an effort to differentiate between the abrasivity of different types of exhaust particles and to determine at what threshold hardness the particles no longer scratch the surface.

Fig. 6. Scratch in copper surface produced by unburned coal fuel particle.

Rotating Pin-on-Disk Wear Test Results

The geometry of the rotating pin-on-disk test machine is shown in Fig. 7. The conventional pin-on-disk machine employs a fixed pin which is pressed against a rotating disk at some prescribed load. In the test used here, both the pin and the disk are rotated by parallel but offset shafts. Both shafts rotate in the same direction but at slightly different speeds. This causes the pin to follow a crisscrossing helical path over the surface of the disk. Sliding on the pin is omnidirectional and the length of the path on the disk is many times greater than would be the case for a fixed pin with the same size disk. A more detailed description of the rotating pin-on-disk test can be found in reference 3.

The test conditions and materials were as follows: The pins were 3/8 inch diameter, commercial, 52100 steel bearing balls with a nominal hardness of 62 HRC. The disks were O-2 tool steel heat treated to a hardness, also, of 62

Fig. 7. Rotating pin-on-disk test geometry.

HRC. The test surface of the disk was surface ground and then polished with 15 μm diamond abrasive. White paraffinic mineral oil with a viscosity of 335-365 SUS was employed as a lubricant in all tests, with or without abrasives. A load of 15 N was applied to the pin and the sliding speed was approximately 60 m/s. The tests were conducted in air at a temperature of $22 \pm 1^\circ\text{C}$ with a relative humidity of about 60%.

In general, the test procedure consisted of conducting one or more runs with mineral oil without abrasives and then following with several tests using mineral oil containing the desired abrasive.

Wear was determined by measuring the diameter of the scar on the pin (bearing ball). Wear volume was computed on the assumption that the scar was flat. With abrasive particles, especially when the size of the particles exceeded 5 μm , it was often difficult to identify precisely the location of the edge of the scar due to rounding and because of indentation damage that extended far beyond the scar edge. The size of the error that might be attributed to this uncertainty in measurement has not yet been determined, but it is probably less than the test-to-test scatter from other sources.

Tests have been conducted on several abrasive materials. A brief description of each abrasive is given in Table 3. The various materials were chosen primarily to explore the influence of particle size and hardness. It may be noted that the hardness of quartz, approximately 1200, is about the same as that of the silicates which are

Table 3. Properties of particles used in wear tests.

Quartz (BCR 66)	0.35-2.5 μm (95% by mass in size range)
Quartz (BCR 70)	0.5-12 μm (95% by mass in size range)
Quartz (BCR 67)	3-20 μm (95% by mass in size range)
MgO	2 μm metallographic polishing abrasive
$\alpha\text{-Al}_2\text{O}_3$	1 μm metallographic polishing abrasive

a principal type of mineral contaminant found in coal. MgO has a hardness of about 800 kg/mm^2 , comparable to that of the pin and disk specimen materials, and $\alpha\text{-Al}_2\text{O}_3$ is substantially harder at 2000 kg/mm^2 .

Preliminary results on the different abrasive materials are summarized in Fig. 8a and b. In Fig. 8a it

a

b

Fig. 8. Rotating pin-on-disk wear test results indicating wear rate of 52100 steel pin with various abrasives and different concentrations in mineral oil. a) Linear plot. b) Logarithmic plot.

can be seen that there is a significant effect of particle size on wear rate. At a concentration of 0.5 wt.%, particles less about 2.5 μm in size had little effect on wear rate. With quartz particles in the size range, 3 - 20 μm , the wear rate was increased by more than one hundred times. The data in Fig. 8a are replotted in Fig. 8b on a logarithmic scale. The relatively small effect of the sub-2.5 μm abrasives at the concentration levels studied is clearly indicated.

Test results obtained on the turbine exhaust particulates are shown in Fig. 9. Even at a concentration of 5 wt. % there is little if any detectable effect. An examination of one collection of particles in the SEM showed that they were similar in morphology and size to the diesel exhaust particles, though it seemed that there was a larger fraction of spherical particles. An analysis has not yet been made for the presence of particles that might be harder than 52100 steel. If such particles are present,

Fig. 9. Rotating pin-on-disk wear test results indicating wear of 52100 steel due to different concentrations of coal-fired turbine exhaust particulates.

the data in Fig. 9 suggests that their concentration is quite low and/or the particle size is in a range below about 2.5 μm and therefore, according to the results in Fig. 8, would not result in a significant increase in wear rate under the conditions of the test.

The fact that the addition of turbine particulate material to the lubricating oil did not result in a significant increase in wear rate is not consistent with coal-fueled diesel engine experience. It may be that the turbine particulate is indeed substantially different from the particulate material which enters the ring / liner contact in the diesel. On the other hand the test conditions employed with the rotating pin-on-disk machine may not adequately reflect those in the diesel engine. These factors will be addressed in future work.

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ORNL-3(A) - DEVELOPMENT OF SURFACE TREATMENTS AND ALLOY MODIFICATIONS
FOR CORROSION-RESISTANT OXIDE SCALES

J. H. DeVan

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

The purpose of this task is to develop protective scales on iron-based alloys in mixed-oxidant (oxygen-sulfur) environments for coal-related applications at 500 to 800°C. Important objectives include (1) development of protective oxide scales by modifying oxide chemistry/microstructure to reduce the transport of sulfur through the scales; (2) formation of a sulfur-diffusional barrier under or above the protective scale to minimize the sulfur attack; and (3) study of the effects of alloy chemistry, oxide morphology, and temperature on the breakdown of protective scales.

DISCUSSION OF CURRENT ACTIVITIES

We are evaluating two general approaches for achieving sulfidation-resistant scales. One is to establish a thermodynamically stable oxide film on an alloy or coating substrate and the other is to incorporate alloying elements that will form a thermodynamically stable and slowly growing sulfide phase. The first approach uses Fe₃Al as the model system and evaluates the effects of alloying modifications, designed to improve mechanical behavior, on oxidation/sulfidation resistance. The second approach, as discussed in the preceding report,¹ involves the addition of 9 to 18 wt % niobium, a strong sulfide former, to improve the sulfidation resistance of alumina-forming iron-based alloys. Work during this reporting period focused on Fe₃Al and derivative alloys, with particular emphasis on the effects of chromium additions on sulfidation behavior. Further details concerning fabrication and mechanical properties of these alloys can be found in "ORNL-2(F) - Development of Iron Aluminides" (this report).

The alloying additions investigated included combinations of the following elements (at. %): Al (26–40%), Cr (2–10%), Mo (0.5%), Nb (1%), Y (0.03%), Zr (0.12%), and B (0.1%). Tests were conducted at 700 and 800°C in $H_2S-H_2-H_2O$ -Ar gas mixture flowing at 150 cm³/min. Compositions of the mixtures at the respective test temperatures together with the activities of oxygen and sulfur are given in Table 1.

Weight changes of the baseline Fe₃Al composition (Fe-28 at. % Al) in the 800°C reference gas mixture (Table 1) are compared in Fig. 1 with the equivalent data for Fe-25Cr-20Ni and Fe-18Cr-6Al (by weight). The weight changes are much less for the former than for the latter two alloys and indicate the formation of a highly protective corrosion product film. Figure 2 shows the scale formed on the Fe-28Al specimen. Although relatively thin, much of the scale spalled from the surface on cooling to room temperature. Areas where spalling has occurred revealed little corrosion of the underlying metal substrate, as evidenced by the fine scratches produced during specimen preparation which still appear sharp and clear. Likewise, the underside (metal side) of the scale shows little porosity and, except for scratches matching those of the metal, is relatively flat and smooth. Energy-dispersive X-ray (EDX) spectroscopy analyses of the gas side and metal side of the corrosion product scale show aluminum to be the major cationic species with only trace amounts of iron or sulfur. X-ray diffraction patterns of the scale match those of γ -Al₂O₃.

Table 1. Test environments generated using $H_2S-H_2-H_2O$ gas mixtures

Percent H ₂	Percent H ₂ S	Percent H ₂ O	Percent Ar	log P _{S₂}	log P _{O₂}
<i>Mixtures used at 800°C</i>					
8.4	0.55	1.46	89.6	-6.0	-20.0
14.1	0.95	2.46	82.5	-6.0	-20.0
79.4	5.4	1.44	13.8	-6.0	-20.0
<i>Mixtures used at 700°C</i>					
0.97	0.184	0.26	98.6	-6.0	-22.0
9.27	17.61	2.37	70.8	-4.0	-22.0

Fig. 1. Weight changes of Fe_3Al binary alloy compared to Fe-Cr-Ni and Fe-Cr-Al alloys.

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Fig. 2. Appearance of corrosion product scale formed on Fe-28Al at 800°C .

The addition of chromium to the Fe-28Al base composition adversely affects the resistance to $\text{H}_2\text{S-H}_2\text{-H}_2\text{O}$ at chromium levels above 2 at. %. Weight changes for ternary alloys containing 2, 4, and 10 at. % are compared with the binary base alloy in Fig. 3. At the higher chromium levels, weight gains after 100 h at 800°C are over 20 times those of the binary alloy, while the 2% alloy shows no difference from the binary composition. Corrosion product scales formed on the 4% and 10% chromium alloys were considerably thicker than on the binary or 2% alloy and were overgrown with multifaceted platelets, as shown in Fig. 4. The surface underlying the scale also appears pockmarked, although the initial surface scratches are still discernable. EDX analyses of the platelets at the scale-gas interface confirm them to be mixtures of iron and chromium sulfides, while the underlying scale areas contain predominantly aluminum and sulfur. X-ray diffraction patterns show the expected Cr_2S_3 pattern but, in addition, contain strong lines for the Al_2S_3 compound. No lines corresponding to either α - or γ - Al_2O_3 were detectable, and it can be concluded that the latter phase must comprise less than 10% of the scale mass.

The corrosion effects of niobium and molybdenum alloying additions were also evaluated in $\text{H}_2\text{S-H}_2\text{-H}_2\text{O}$ mixtures at 800°C . Additions of 1 at. % niobium and 2 at. % molybdenum to the Fe-28Al alloy reduced the corrosion rate over a 100-h period by factors of 2 and 4, respectively. The addition of 1% niobium also lowered the corrosion rate of alloys containing 4% chromium, as shown in Fig. 5, although the niobium addition did not change the character of the scale (predominantly sulfides). Some reduction in weight change of alloys with 4% chromium was effected by the addition of 0.3% yttrium and 0.12% zirconium, but the reduction was less than for the 1% niobium addition (Fig. 5).

The adverse effect of chromium at the 4% level can be offset by increasing the aluminum concentration to 40 at. %. As shown in Fig. 5, comparable weight changes were recorded for the Fe-28Al and Fe-40Al-4Cr alloys after one week at 800°C , and the scale formed on the latter alloy was typical of Fe_3Al alloys containing no chromium (Fig. 2).

Fig. 3. Effect of chromium additions on weight change of Fe₃Al at 800°C.

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Fig. 4. Scale formed on Fe-2% Al-4% Cr after 20 h at 700°C.

Fig. 5. Effect of minor alloying additions on weight changes on Fe₃Al alloys containing 4% chromium.

In view of the susceptibility to scale spallation of the Fe₃Al alloy, thermal cycling effects on oxidation-sulfidation resistance are of concern. However, in thermal cycling experiments to date, the binary alloys have shown no major deterioration in corrosion performance. This is evident in Fig. 6, which compares the weight change behavior of Fe-28Al exposed isothermally at 800°C with a similar specimen thermally cycled from 800°C to room temperature every 48 h. Although some scale loss appears to have occurred during thermal cycling (reflected in the lower overall weight gain), there was no change in the final scale appearance or any evidence of sulfide phases in the scale or on the metal surface. All of these results suggest that the initial nucleation and growth of Al₂O₃ is extremely fast compared to that of iron sulfide, and that either this comparative difference in growth rate holds even with repeated scale detachment or that, once established, some residuum of the Al₂O₃ scale remains coherent with the substrate metal even though the greater part of the scale may be detached. The relatively high bulk aluminum concentration of the alloy may also be a key factor in maintaining a sufficiently

Fig. 6. Effect of thermal cycling on weight change of Fe-28Al alloy at 800°C. (Thermally cycled to room temperature every 48 h).

high aluminum level at the surface to sustain the selective oxidation process on which Al_2O_3 formation depends.

Adding chromium to the Fe₃Al alloy significantly changes the corrosion product scale and, attendantly, the corrosion rate in H_2S - H_2 - H_2O mixtures. Above a level of 2% chromium, the scale changes from a thin, smooth Al_2O_3 oxide film to a thicker, sulfide-containing scale comprised of Cr_2S_3 platelets growing out of an Al_2S_3 + Al_2O_3 layer. This scale is also very prone to spalling on cooling. Studies conducted on these latter scales thus far have been inconclusive as to whether the effect of chromium is to simply increase the diffusion of sulfur by changing the defect concentration of an otherwise protective Al_2O_3 oxide film, or to "trigger" the growth of chromium sulfide nodules as mechanical defects develop in the oxide scale. Minor additions of niobium and, to a lesser extent, zirconium and yttrium appear to improve the sulfidation resistance of the chromium-containing alloys. Again, it has not yet been determined whether the action of these additions is manifested in the defect structure or in the mechanical integrity of the scales.

Although the presence of chromium significantly affects the sulfidation of the Fe-28Al alloy, the corrosion rate is still considerably below that of the Fe-18Cr-5Al (12 at. % Al) alloy at 700 and 800°C. On further increasing the aluminum content to 40 at. %, the adverse effect of chromium at the 4% level is effectively suppressed. This suggests that aluminizing the near surface region to a level of ≥ 40 at. % (commensurate with FeAl structure) may be an expedient method for improving sulfidation resistance should chromium prove indispensable as an alloying addition.

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ORNL-3(B) - IN-SITU SCANNING ELECTRON MICROSCOPY STUDIES
OF EROSION AND EROSION-CORROSION

J. R. Keiser

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

The purpose of this study is to investigate the processes of corrosion, erosion, and erosion-corrosion in coal combustion and conversion environments. As part of this work, we are performing in situ scanning electron microscopy studies of the erosion, corrosion, and simultaneous erosion and corrosion of hot metallic samples.

DISCUSSION OF CURRENT ACTIVITIES

Fundamental studies are currently being conducted on mechanisms of erosion and corrosion, and long-range plans call for studies of erosion-corrosion. During this period, several studies have been conducted. One study involves determination of the variation in hardness beneath the surface of four aluminum alloys that have been subjected to multiple impacts by spherical erosive particles. Another study involves similar hardness measurements on annealed 1100 aluminum samples that were exposed to erosive particle impacts at a level below that required to reach steady state conditions. The samples were all given different levels of exposure to permit study of the changes that occur as a steady state condition is reached. A third study involves use of the erosive particle gun to impact the surface of previously oxidized materials that have small differences in base metal composition. A cooperative study of erosion-corrosion of selected materials has been initiated with Lawrence Berkeley Laboratory.

The manner in which the energy imparted to a material by a high-velocity impact is actually manifested in the target material has been the subject of considerable controversy. On the assumption that a significant portion of the energy is retained near the surface in the form of heat, annealing or even melting of the surface has been suggested. Because of

the significant plastic deformation and the assumption that heat rapidly diffuses into the bulk of the target material, extensive hardening of the surface of the target material has also been suggested.

The erosion study of aluminum has utilized four alloys with significantly different mechanical properties. These alloys are annealed 1100 aluminum, 50% cold-worked 1100 aluminum, 6061-T6 alloy, and 7075-T6 alloy. Two sets of samples of these alloys were prepared; one set was subjected to single 30° impacts by 343- μm -diam tungsten carbide balls at 30 m/s, and a second set was sent to Lawrence Berkeley Laboratory to be eroded by a stream of 400 to 600 μm steel shot at an impact angle of 30° and a velocity of about 55 m/s. Results from studies with the first set of samples have been published in the open literature.^{1,2} The second set of samples has been sectioned and hardness data collected; the results provide some new information about the effects of multiple-particle impacts.

In this second set of samples that was exposed to multiple-particle impacts, a rippled surface was developed. A cross section shows troughs and waves with a crest developed on some of the waves. Hardness measurements were made below the trough in each of the samples, and measurements were also made through the full height of a wave in the annealed 1100 aluminum sample. Results of the measurements in the wave troughs are shown in Figs. 1-4. These results indicate that hardening occurs in all the samples, but only to a depth about the same as that seen in the single impacts on the same materials. For the measurements made in the wave crest, it was found that hardening occurs and extends to a much greater depth (Fig. 5). In fact, the hardening below the wave crest extends to about the same depth below the original surface as seen for the trough. This suggests that there is a relatively flat region of unaffected material above which is a layer of rippled material that was affected by the particle bombardment.

Similar studies are currently being performed on the samples exposed to different "doses" of erosive particles. Results of these studies will be presented in the next report and will be submitted for open literature publication.

The mechanical response of preformed oxide scales to energetic particle bombardment is being studied in the modified scanning electron

Fig. 1. Relative hardness versus depth below the surface for annealed 1100 aluminum eroded by a stream of 400 to 600 μm steel shot at an impact angle of 30° and a velocity of about 55 m/s.

Fig. 2. Relative hardness versus depth below the surface for cold worked 1100 aluminum eroded by a stream of 400 to 600 μm steel shot at an impact angle of 30° and a velocity of about 55 m/s.

Fig. 3. Relative hardness versus depth below the surface of 6061-T6 aluminum eroded by a stream of 400 to 600 μm steel shot at an impact angle of 30° and a velocity of about 55 m/s.

Fig. 4. Relative hardness versus depth below the surface for 7075-T6 aluminum eroded by a stream of 400 to 600 μm steel shot at an impact angle of 30° and a velocity of about 55 m/s.

Fig. 5. Relative hardness versus depth below the surface for annealed 1100 aluminum eroded by a stream of 400 to 600 μm steel shot at an impact angle of 30° and a velocity of about 55 m/s showing the greatly increased depth of hardening below the wave crest. Note the significantly greater depth over which hardening occurs in the wave crest compared to the wave valley.

microscope using a technique called Impact Response of Oxide Scales (IROXS). A report describing the preliminary studies has been written.³ The purpose of this work is to increase our knowledge of the means by which small concentrations of rare earth or reactive elements improve the adherence of oxide scales to certain alloys.

Our studies will characterize the response to high-velocity impacts of preformed oxide scales in terms of (1) the propensity for deformation and cracking, (2) crack growth, and (3) the tendency for cracks to heal. The initial studies consisted only of observations of deformation and cracking propensity on impacts made at room temperature on alloys of two different compositions: a chromia-forming alloy Fe-20Cr-25Ni-0.7Nb (wt %) with and without addition of 0.13% Ce obtained from Harwell Laboratory, United Kingdom, and an alumina-forming alloy Ni-20Cr-12Al containing 0.05, 0.1, 0.5, 1.0 or 3.0% Y obtained from United Technologies Research Center, East Hartford, Connecticut. More thorough and extensive studies are now under way and will be described in a subsequent report.

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PITT-3 - CORROSION MECHANISMS OF COAL COMBUSTION
PRODUCTS ON ALLOYS AND COATINGS

G. M. Kim, E. A. Gulbransen and G. H. Meier

Department of Materials Science and Engineering
848 Benedum Hall
University of Pittsburgh
Pittsburgh, PA 15261

INTRODUCTION

This program is intended to generate an improved understanding of mixed oxidant corrosion which may be used in interpreting the behavior of alloys and coatings in the atmospheres typical of coal conversion processes. The study is concentrating on two closely related tasks, (1) thermodynamic and kinetic modelling of mixed oxidant corrosion of alloys and (2) experimental studies of mixed oxidant corrosion.

In the area of modelling the existing thermochemical and kinetic (diffusivities, rate constants etc.) data are being used to model the corrosion of binary alloys in mixed oxidants (O, S, Cl, C). This is being done by constructing the appropriate stability diagrams with the aid of computer techniques and then using the kinetic data to predict a reaction path for the corrosion process. As work proceeds more complicated systems (e.g. ternary alloys) will be treated.

In the experimental area the factors affecting the degradation of protective oxide layers (Cr_2O_3 , Al_2O_3 , SiO_2) in atmospheres containing oxygen, sulfur, carbon and chlorine are being investigated. A wide range of experimental techniques will

be brought to bear to allow evaluation of the chemical, physical and metallurgical factors involved in the degradation mechanisms. As experimental data are obtained they will be fed back into the kinetic models to refine them.

DISCUSSION OF CURRENT ACTIVITIES

This project has been completed and a Draft Final Report has been submitted for review.

UCB-3 - SOLID PARTICLE EROSION IN TURBULENT FLOWS PAST TUBE BANKS

J.A.C. Humphrey, R. Greif, M.O. Schweitzer and L. Smith

Department of Mechanical Engineering
The University of California at Berkeley
Berkeley, California 94720

INTRODUCTION

During this period of research, attention has focused on completing the remaining objectives of the research contract. These consist in predicting non-isothermal flows past tubes and the effects of temperature gradients on particle paths as well as the attendant consequences to erosion where particles collide with tubes. In parallel, we have been exploring the use of a new apparatus for developing experimental techniques to study fluidized particle flows around tubes. The apparatus is very simple to construct and allows some of the main fluid mechanic features of fluidized beds to be clearly visualized and quantified optically.

DISCUSSION OF CURRENT ACTIVITIES

Calculation of Non-Isothermal Flows Past Tubes

The isothermal laminar and turbulent flow fields obtained by Schuh¹ (see, also, Schuh et al.²) are being used to solve the energy transport equation to obtain the temperature distributions around hot (cold) tubes in cold (hot) gas streams. This approach implies the existence of a forced convection condition, wherein it is appropriate to assume that (for all practical purposes) density and the transport

properties are constant; i.e., they do not depend on temperature. Notwithstanding, to evaluate the first order effect of temperature on particle trajectories, the calculated temperature field is used to calculate a corresponding non-uniform viscosity field. It is this viscosity (which varies with temperature according to position in space) that is then used to evaluate the drag force acting on any given particle.

Currently, non-isothermal laminar flows past tubes have been predicted successfully. For example, very good agreement has been found between measurements and calculations of the circumferential distribution of the Nusselt number. Corresponding accurate results for turbulent flow have not yet been obtained due to difficulties experienced with the turbulence model used. This employs law-of-the-wall relationships to derive the turbulent shear stress and heat flux distributions in the wall layer around the tube. Such an approach yields inaccurate predictions of the heat transfer, especially near the separation point. Efforts are underway to refine the turbulence model in this region of the flow.

With the flow, temperature and variable viscosity fields in hand, calculations will be made to systematically evaluate the influence of temperature (through viscous drag) on particle trajectories and tube erosion. The deterministic and stochastic approaches to be used are respectively described in Schuh et al.²

Experimental Apparatus for Studying Concentrated Particle-Fluid Flows

The study of fluidized beds is hampered by the optical inaccessibility of these concentrated particle flows. When probes are introduced instead, to monitor field variables, they are easily damaged or perturb the flow. We have been concerned with developing a test-section that emphasizes the two-dimensional aspects of concentrated particle-fluid motions and allows optical probing. The device in question consists of two transparent plexiglas plates of rectangular

cross-section (roughly $30 \times 90 \text{ cm}^2$) brought very closely together with a 4 mm spacing between them and sealed along their periphery, to allow the motion of a mixture of fluid and solid glass spheres in the gap space. A circular cut through the plates, with a transparent plexiglas O-ring to seal the particle suspension in the gap region, simulates the presence of a tube. The transparent circular wall allows direct observations to be made of the solid-fluid motions immediately adjacent to it. This is precisely where it is of most interest to know the particle and fluid flow fields.

Figure 1 shows the test section resting on a jig where it can be quickly turned upside down with a 180° rotation. Upon rotation, the particle bed which is initially below the fluid (in the present case water) ends up above it. In this position the particle bed is unstable and particles commence detaching from the particle bed-water interface. The detachment process and the ensuing motion have been described by Humphrey and Schuler³ and Humphrey et al.⁴ In those experiments there was no hole in the plates, as shown in Fig. 1, to simulate the presence of a tube. (Emphasis was placed instead on understanding the character of the particle-fluid motion at the unstable bed-fluid interface.)

Figure 2 shows the type of motion that is induced soon after inverting the test section in the jig. Particle-laden plumes detach from the bed-liquid interface and fall past the circular insert. The character of the motion is strongly dependent on the liquid viscosity, the relative densities of the two phases and the particle size. (In these experiments pure water and glass spheres of diameter 149-177 μm were used.) Figure 3 is a close up view of the suspended flow past the circular insert, at a later time. A layer of particles has accumulated above the cylinder and a layer of water devoid of particles appears below it. An instability is observed where the slurry-water layers meet at about 90° from the vertical around the cylinder. The instability is caused by the relative shearing action of these two layers.

Experiments in this test section are underway for a range of fluid viscosities and particle sizes. The objective is to develop optically based experimental techniques that will allow measurements to be obtained in a subsequent test section modified to simulate a fluidized bed condition more realistically. Thus, in the new device a vertical throughflow of liquid (or air) will be allowed, to maintain the solid phase in suspension indefinitely.

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Figure 1. The test section.

Figure 2. Particle-liquid flow at early time.

Figure 3. Particle-liquid flow past "tube".

UCIN-3 - STUDY OF PARTICLE REBOUND CHARACTERISTICS
AND MATERIAL EROSION AT HIGH TEMPERATURES

W. Tabakoff, A. Hamed and H. Eroglu

Department of Aerospace Engineering and Engineering Mechanics
University of Cincinnati
Cincinnati, Ohio 45221

INTRODUCTION

The objective of this research work is to investigate the basic erosion processes and fluid mechanics associated with material degradation in the components of various coal conversion and utilization systems. The understanding of erosion patterns and rates will be enhanced through a study of the rebound characteristics of particles impinging various surfaces and through the measurement of erosion rates of materials exposed to high temperatures. The overall goal is to develop a quantitative model, which will facilitate the prediction of erosion in systems operating in particulated environments.

DISCUSSION OF CURRENT ACTIVITIES

Background

The use of pulverized coal as fuel in many power plants and industrial establishments is inevitable both in the present and in the future. The major problem confronting earlier developers of coal-burning turbines is the serious erosion of turbine blades and other metal parts by the suspension of fly ash in hot combustion gases.

Under two-phase flow conditions, the gas and particles experience different degrees of turning as they flow through the blade channels. This is mainly due to the difference in their inertia. This results in a concentration gradient across the blade channel and causes a change in the properties of gas and particles. The net result is a change in the blade surface pressure distribution, which alters the engine performance during the period of particle ingestion.

In the case of erosive particles, a permanent loss of performance is associated with the surface erosion, which is caused by particle surface

impacts. The performance loss depends upon the location and the condition of the deteriorated surfaces. These are critical to the aerodynamic performance of turbine blades which are particularly sensitive to the blade leading and trailing edge configuration and the condition of the blade suction surface. Computer codes are used to model the particle dynamics in turbomachinery flow fields through the various blade rows, and to determine the particle impact conditions with the various surfaces which affect their erosion. The codes however require empirical equations for particle restitution characteristics to represent the effects of particle surface interactions on the particle trajectories and the resulting surface erosion.

The restitution coefficients are influenced by the particles and target characteristics and by the particle impact conditions relative to the target surface. References [1] through [9] reported the results of this experimental program to study the effect of target and particle materials, particle size, particle velocity, and the target surface shape on the particle rebound characteristics. Empirical equations for the particle restitution parameters were developed for use in the particle trajectory and erosion computer codes. All the results reported in [1] through [9] were obtained using a two-component Laser Doppler Velocimeter (LDV) system described in references [1] through [4]. The two-dimensional particle velocity measurements were conducted in the plane of the impinging particle velocity and the normal to the target surface. This plane is the xz plane in Fig. 1, where the rebound velocity components V_{N2} and V_{T2} , and the impact velocity components V_{N1} and V_{T1} were measured. That precluded any particle rebound velocity components which are perpendicular to that plane. Later, the particle rebound velocities in the y direction such as V_{y2} in Fig. 1 were measured using a three-component LDV system for INCO 718 target material, and the results are reported in reference [10].

In the period between April 1 and September 30, 1988, first, three-dimensional LDV measurements of the rebound characteristics were performed for 15 micron mean diameter fly ash particles impacting 2024 aluminum

target material. The results of these measurements are presented in this report. Later, two-dimensional particle rebound characteristics were measured at small impact angles (less than 15 degrees) for 15 micron mean diameter fly ash particles impacting 410 stainless steel, 2024 aluminum, 6Al-4V titanium, INCO 718, RENE 41, AM355, L605 cobalt and alumina (Al_2O_3) target samples. The data for the first four materials (410 stainless steel, 2024 aluminum, 6Al-4V titanium and INCO 718) was analyzed, and combined with the previous restitution coefficients in order to extend the range of these restitution parameters to smaller impact angles. The new rebound correlations for these first four target materials are presented in this report. The data for the remaining four materials is being analyzed, and the results of the analysis will be presented in the final technical report.

Experimental Set-Up

The experimental set-up consists of the erosion wind tunnel, the LDV system, the data acquisition system and the particle feeder. A detailed description of the wind tunnel and the particle feeder is given in Ref. [11]. The two-component LDV system used in the measurement of the restitution characteristics at small impact angles is described in references [1] through [4]. The three-component LDV system used in the measurement of the third rebound velocity for 2024 aluminum target material is described in references [10] and [12].

Results

The particle rebound experiments were conducted for 15 micron mean diameter fly ash particles impacting target samples of various materials. The composition and size range of fly ash particles, and the properties for some of the target materials are given in [1]. The measurements were obtained at 0.5mm distance from the sample surface in all the tests. Figure 1 illustrates the 3-D impact geometry for the measurements. The experiments were conducted at a particle impact velocity of 320 ft/s (98 m/s) which was measured at the center of the tunnel cross-section. The uncertainties associated with the measurements of this report are the same as in reference [1].

During the experiments, the 2024 aluminum target sample was rotated around the y-axis to change the impact angle β_1 in the XZ plane as shown in Fig. 1. Since the 2-D rebound characteristics in the XZ plane are reported in a the next section, the present discussion will be restricted to the third rebound velocity in the y-direction, i.e., normal to the XZ plane. In the results, the third particle rebound velocity component, V_{Y2} , is considered for only one side of the XZ plane because of symmetry.

Figures 2 and 3 present the effect of the particle impingement angle on the third particle rebound velocity component V_{Y2} and angle α_2 respectively for 2024 aluminum target material. Figure 2 shows the variation of V_{Y2} with the impact angle β_1 , and a straight line fit of $V_{Y2} = 47$ ft/sec is obtained for the experimental data at all impact angles, which indicate that V_{Y2} is insensitive to the changes in β_1 . Figure 3 shows the variation of α_2 with β_1 for 2024 aluminum. Since V_{Y2} is not affected by β_1 , the variation of the particle tangential rebound velocity V_{T2} in the XZ plane is responsible for the behavior, reflected in Fig. 3.

Based on these and the results of reference [10], new restitution parameters were defined to modify the previously reported 2-D results. These are labeled the third velocity restitution ratio ($e_Y = V_{Y2}/V_{T1}$) and the second directional coefficient ($e_\alpha = \alpha_2/\beta_1$) respectively. Figures 4 and 5 show the variation of these new restitution parameters with the impact angle β_1 for 2024 aluminum. Figures 6 and 7 compare e_Y and e_α distributions for INCO 718 and 2024 aluminum target materials. It appears that these new restitution coefficients are not so sensitive to target material difference.

The actual 3-D tangential velocity restitution ratio can be obtained, by combining the 2-D value with the newly defined third velocity restitution ratio as follows:

$$e'_T = \sqrt{e_T^2 + e_Y^2} \quad (1)$$

Fig. 2. Influence of Impingement Angle on the Out-of-Plane (Third) Velocity Component.

Fig. 3. Influence of Impingement Angle on the Out-of-Plane Direction α_2 .

Fig. 4. Influence of Impingement angle on the Out-of-Plane (Third) Velocity Restitution Ratio.

Fig. 5. Influence of Impingement Angle on the Out-of-Plane (Second) Directional Coefficient.

Fig. 6. Comparison for the Influence of Impingement Angle on the Out-of-Plane (Third) Velocity Restitution Ratio.

Fig. 7. Comparison for the Influence of Impingement Angle on the Out-of-Plane (Second) Directional Coefficient.

where e_T' is the actual 3-D tangential restitution ratio. Referring to Fig. 1, this can be written in terms of the velocity components as follows

$$e_T' = \frac{\sqrt{V_{T2}^2 + V_{Y2}^2}}{V_{T1}} = \frac{V_{T2}'}{V_{T1}} \quad (2)$$

The 3-D tangential restitution ratio e_T' as determined from equation (1), is plotted in Figure 8 for 2024 aluminum, together with e_T as determined by the 2-D measurements. Figure 8 shows a small difference between e_T and e_T' . One should also remember that due to symmetry, only about half of the particles rebound in a given direction (+y), while the other half rebound in the opposite direction from the XZ plane (-y).

Fig. 8. Influence of Impingement Angle on the Tangential Velocity Restitution Ratio.

The following least squares polynomial curve fit expression was obtained for the 3-D tangential restitution ratio for 2024 aluminum:

$$e_T' = \frac{V_{T2}'}{V_{T1}} = 1.05703 - 2.40821 \beta_1 + 7.85254 \beta_1^2 - 10.29148 \beta_1^3 + 4.48019 \beta_1^4 \quad (3)$$

where β_1 is in radians.

Small Impact Angles

The particle trajectory calculations in the gas turbine combustion chambers [13] showed that, the particle impact angle with the chamber walls can be very small for fly ash particles. However, experimental data for the restitution ratios was previously obtained for the impact angle, β_1 , range of 15 to 75 degrees. The information about the restitution ratios out of this range were obtained by extrapolation. In order to increase the accuracy of the restitution ratios at small impact angle range, LDV measurements of impact and rebound velocities were performed for 5 and 10 degrees impact angles. The restitution ratios at these small angles were determined for 410 stainless steel, 2024 aluminum, 6Al-4V titanium and INCO 718 in this report. Combining these new data with the previous restitution ratios, least squares polynomial curve fits of the mean values of the restitution parameters were obtained. These curve fits are shown as solid lines in figures 9 through 24 together with the experimental points.

The total velocity restitution ratio, V_2 / V_1 , is plotted against the impact angle β_1 in Figs. 9, 13, 17 and 21 for 410 stainless steel, 2024 aluminum, 6Al-4V titanium and INCO 718, respectively, covering an impact angle range of 5 to 75 degrees.

The directional coefficient, β_2 / β_1 , is plotted against impact angle β_1 in Figs. 10, 14, 18 and 22 for the same four materials.

The normal, V_{N2} / V_{N1} , and the tangential, V_{T2} / V_{T1} , restitution ratios are also plotted against the impact angle β_1 . The plots for the

normal restitution ratios for these materials are shown in Figs. 11, 15, 19, and 23. The tangential restitution ratios versus impact angle plots are given in Figs. 12, 16, 20 and 24.

The new normal restitution ratio and directional coefficients at small (less than 15 degrees) impact angles show significant differences from the previous values, if the Figs. 10-11, 14-15, 18-19, and 22-23 are compared with Figs. 19-20, 27-28, 31-32, and 39-40 of reference [1] respectively.

The following empirical equations represent the variation of the restitution parameters with the impingement angle β_1 according to the curve fits of Figs. 9 through 24.

410 Stainless Steel:

$$e_V = v_2/v_1 = 0.76 + 2.01\beta_1 - 7.66\beta_1^2 + 8.11\beta_1^3 - 2.72\beta_1^4 \quad (4a)$$

$$e_\beta = \beta_2/\beta_1 = 0.15 + 3.85\beta_1 - 8.64\beta_1^2 + 7.49\beta_1^3 - 2.25\beta_1^4 \quad (4b)$$

$$e_N = v_{N2}/v_{N1} = 0.08 + 4.27\beta_1 - 11.19\beta_1^2 + 10.42\beta_1^3 - 3.24\beta_1^4 \quad (4c)$$

$$e_T = v_{T2}/v_{T1} = 0.88 + 0.44\beta_1 - 1.43\beta_1^2 - 0.18\beta_1^3 + 1.02\beta_1^4 \quad (4d)$$

2024 Aluminum:

$$e_V = v_2/v_1 = 0.85 + 1.20\beta_1 - 5.34\beta_1^2 + 5.86\beta_1^3 - 2.04\beta_1^4 \quad (5a)$$

$$e_\beta = \beta_2/\beta_1 = 0.67 - 4.34\beta_1 + 27.10\beta_1^2 - 58.41\beta_1^3 + 52.14\beta_1^4 - 16.39\beta_1^5 \quad (5b)$$

$$e_N = v_{N2}/v_{N1} = 0.26 + 2.15\beta_1 - 6.06\beta_1^2 + 6.44\beta_1^3 - 2.33\beta_1^4 \quad (5c)$$

$$e_T = v_{T2}/v_{T1} = 0.56 + 6.26\beta_1 - 31.93\beta_1^2 + 63.15\beta_1^3 - 54.38\beta_1^4 + 17.01\beta_1^5 \quad (5d)$$

6Al-4V Titanium:

$$e_V = v_2/v_1 = 0.85 + 1.39\beta_1 - 7.40\beta_1^2 + 9.68\beta_1^3 - 3.78\beta_1^4 \quad (6a)$$

$$e_\beta = \beta_2/\beta_1 = 0.51 + 1.89\beta_1 - 4.74\beta_1^2 + 4.57\beta_1^3 - 1.48\beta_1^4 \quad (6b)$$

$$e_N = v_{N2}/v_{N1} = 0.41 + 2.88\beta_1 - 10.06\beta_1^2 + 11.68\beta_1^3 - 4.30\beta_1^4 \quad (6c)$$

$$e_T = v_{T2}/v_{T1} = 0.91 + 0.61\beta_1 - 4.37\beta_1^2 + 5.87\beta_1^3 - 2.03\beta_1^4 \quad (6d)$$

Fig. 9. Influence of Impact Angle on the Erosive Particle Velocity Restitution Ratio for 410 Stainless Steel.

Fig. 10. Influence of Impact Angle on the Erosive Particle Directional Coefficient for 410 Stainless Steel.

Fig. 11. Influence of Impact Angle on the Erosive Particle Normal Velocity Restitution Ratio for 410 Stainless Steel.

Fig. 12. Influence of Impact Angle on the Erosive Particle Tangential Velocity Restitution Ratio for 410 Stainless Steel.

Fig. 13. Influence of Impact Angle on the Erosive Particle Total Velocity Restitution Ratio for 2024 Aluminum.

Fig. 14. Influence of Impact Angle on the Erosive Particle Directional Coefficient for 2024 Aluminum.

Fig. 15. Influence of Impact Angle on the Erosive Particle Normal Velocity Restitution Ratio for 2024 Aluminum.

Fig. 16. Influence of Impact Angle on the Erosive Particle Tangential Velocity Restitution Ratio for 2024 Aluminum.

Fig. 17. Influence of Impact Angle on the Erosive Particle Total Velocity Restitution Ratio for 6Al-4V Titanium.

Fig. 18. Influence of Impact Angle on the Erosive Particle Directional Coefficient for 6Al-4V Titanium.

Fig. 19. Influence of Impact Angle on the Erosive Particle Normal Velocity Restitution Ratio for 6Al - 4V Titanium.

Fig. 20. Influence of Impact Angle on the Erosive Particle Tangential Velocity Restitution Ratio for 6Al - 4V Titanium.

Fig. 21. Influence of Impact Angle on the Erosive Particle Total Velocity Restitution Ratio for INCO 718.

Fig. 22. Influence of Impact Angle on the erosive Particle Directional Coefficient for INCO 718.

Fig. 23. Influence of Impact Angle on the Erosive Particle Normal Velocity Restitution Ratio for INCO 718.

Fig. 24. Influence of Impact Angle on the Erosive Particle Tangential Velocity Restitution Ratio for INCO 718.

INCO 718:

$$e_V = V_2/V_1 = 0.94 - 1.39\beta_1^2 + 1.99\beta_1^3 - 0.87\beta_1^4 \quad (7a)$$

$$e_\beta = \beta_2/\beta_1 = 0.52 + 0.34\beta_1 + 0.78\beta_1^2 - 2.49\beta_1^3 + 1.26\beta_1^4 \quad (7b)$$

$$e_N = V_{N2}/V_{N1} = 0.47 + 0.61\beta_1 - 1.58\beta_1^2 + 1.31\beta_1^3 - 0.43\beta_1^4 \quad (7c)$$

$$e_T = V_{T2}/V_{T1} = 0.95 - 0.13\beta_1 - 0.52\beta_1^2 + 0.89\beta_1^3 - 0.18\beta_1^4 \quad (7d)$$

where β_1 is measured in radians and these equations are valid within the impact angle range 5-75 degrees.

Conclusions

The out-of-plane (third) component rebound characteristics were determined for 2024 aluminum impacted by 15 microns mean diameter fly ash particles. They were insensitive to the changes in impact angle β_1 . The magnitude of 3-D tangential velocity restitution ratio did not differ much from the 2-D magnitude, however, its effect on the erosion rate distribution should be investigated.

The range of experimental particle rebound data was extended to smaller impact angles (5-15 degrees) which are frequently encountered in combustion chambers. New expressions were derived for the restitution characteristics combining the new experimental data for the smaller impact angles with the previous data. These expressions were obtained for 410 stainless steel, 2024 aluminum, 6Al-4V titanium and INCO 718, and are valid within the impact angle range of 5-75 degrees.

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**UES-3 - INVESTIGATION OF THE EFFECTS OF MICROALLOY CONSTITUENTS,
SURFACE TREATMENTS, AND OXIDATION CONDITIONS ON THE DEVELOPMENT
AND BREAKDOWN OF PROTECTIVE OXIDE SCALES**

V. Srinivasan

Universal Energy Systems, Inc.
4401 Dayton-Xenia Road
Dayton, Ohio 45432

INTRODUCTION

The primary objective of this program is to understand and gain control over the factors that promote the formation of adherent corrosion-resistant protective chromia and alumina scales for long term application in coal combustion and gasification environments. It has been planned to achieve this objective by investigating the effects of minor alloy additions, surface pre-treatments and the oxidation conditions on the process of formation and breakdown of chromia and alumina scales in environments containing oxygen and sulfur. The temperatures of interest are in the range of 500-700°C, and the partial pressures of oxygen and sulfur of the order of 10^{-20} and 10^{-8} atm. respectively. To identify the steps of scale breakdown pre-oxidized samples are exposed to atmosphere of oxygen and sulfur for different lengths of time. A variety of surface analytical instruments is used to characterize the scale and the substrate, and therefore to understand the magnitude and the mechanisms of mixed gas corrosion process.

DISCUSSION OF CURRENT ACTIVITIES

Experimental Materials and Methods

Three base alloys, Fe-25Cr, Fe-25Cr-20Ni and Fe-25Cr-6Al and their derivatives with bulk addition, 1% of Ce, Hf, La, Y, Pt or Si were chosen for the present study. (Chemical compositions are in

wt.% unless otherwise defined.) The base model alloys form chromia or alumina protective scales at high temperatures, and represent the groups of ferrous alloys that are of interest in fossil energy applications. Controlled purity experimental alloys were supplied by a commercial vendor and Ames Laboratory, Ames, Iowa. Their methods of preparation and chemical compositions were given in the previous semiannual reports^{1,2}. All base alloys were given an annealing treatment at 1000°C for 2 hours in flowing Ar. One set of coupons of approximate dimensions, 1 cm x 1 cm 0.1 cm were cut from the annealed base alloy bars. The other set of circular coupons of thickness, 0.1 cm were cut from the as-cast alloy rods of diameter, 1.25 cms. Each coupon had a small hole of diameter, about 0.1 cm for suspension in the reaction tube. The coupons were polished both sides metallographically up to 1 μ m alumina. This surface preparation was maintained as the standard reference finish for all samples.

Isothermal oxidation tests in flowing oxygen were performed using Cahn balances. Isothermal mixed gas corrosion tests and the sequential pre-oxidation-oxidation/corrosion tests were accomplished in a horizontal furnace. The temperature for both types of tests was 700°C. A gas mixture of $H_2/H_2S/H_2O/Ar$ was sent through the reaction section of a quartz tube surrounded by a resistance furnace, and was equilibrated by a platinum auto catalyst located upstream of the samples at the test temperature. The estimated partial pressures of oxygen and sulfur were about 10^{-20} and 10^{-8} atm. respectively at 700°C. Multiple samples up to 16 were exposed simultaneously for times up to 192 hours. Samples were weighed before and after exposure in a Mettler balance with a reproducible accuracy of 0.1 mg. A third set of experiments to characterize the scale in the early stages of its formation and the scale breakdown processes by sulfur is being carried out in more controlled experimental conditions. Two types of experiments, pre-oxidation and pre-oxidation followed by oxidation/sulfidation are being carried out at 700°C on the base alloys and Fe-25Cr-1V. The pre-oxidation run is at $PO_2 = 10^{-20}$ atm., while the oxidation/sulfidation runs are at $PO_2 = 10^{-20}$ and

$PS_2 = 10^{-8}$ atm. The duration of each test is different. A unique feature of this set-up at the Battelle Northwest Laboratories, Richland, WA where the AES study is conducted is that the furnace with the reaction tube is enclosed in a glove box. This glove box is filled with high purity Ar. Samples after exposure in a horizontal furnace are removed from the reaction tube to an "anoxic" container under Ar for transfer to a Perkin-Elmer 560 Multiprobe Surface Analysis system. "Anoxic" transfer prevents the scale/gas interface contamination by the laboratory atmosphere.

Exposed samples, except those run in glove box-furnace, were first visually examined, and later in optical and scanning electron microscope/energy dispersive analysis system, SEM/EDAX. Samples were hot-mounted edge-wise and polished metallographically for cross-sectional metallography of scale/substrate interface. Scale surface (scale/gas interface) and the cross-section (scale/metal interface) were examined using SEM/EDAX. XRD patterns were taken on a few samples to determine the phases present in the scale using $Cu K_{\alpha}$ line and an excitation voltage of 40 KV; 50 mA.

Thin disks of 3 mm in diameter were punched out from the mechanically abraded alloy coupons. They were further polished up to 1 μ m alumina. They were oxidized at 700°C in flowing oxygen in a horizontal furnace for about 2 hours. The oxidized disks were electrolytically thinned from one side by a single jet polishing unit. The electrolyte was BK-2 consisting of 1000 ml methanol, 12 gr. lithium chloride, 24 gr magnesium perchlorate and 200 ml butyl cellosolve. The temperature and voltage were about -50°C and 100 V. When a hole was formed in the disk, the latter was removed from the polishing unit, washed and dried. It was further thinned for a few minutes by ion-milling to improve the quality of electron transparency. Foils thus prepared are being seen in a scanning-transmission electron microscope (STEM) Hitachi-600 to characterize the oxide scales.

Table 1 gives the alloys that have been studied so far.

Table 1 - Test Matrix
Oxidation and Oxidation/Corrosion Tests

Alloy	Oxidation 120 Hrs. ¹	Corrosion ² , Time, Hrs.					
		1	24	48	90-96	144	192
Fe-25Cr	X		X		X	X	X
Fe-25Cr-1Ce					X	X	X
Fe-25Cr-1Hf		X	X	X	X	X	X
Fe-25Cr-1La					X	X	X
Fe-25Cr-1Y		X	X	X	X	X	X
Fe-25Cr-1Pt		X	X	X	X	X	X
Fe-25Cr-3Si		X	X	X	X	X	X
Fe-25Cr-20Ni	X	X		X	X	X	X
Fe-25Cr-20Ni-1Ce		X	X	X	X	X	X
Fe-25Cr-20Ni-1Hf	X			X	X	X	X
Fe-25Cr-20Ni-1La		X	X	X	X	X	X
Fe-25Cr-20Ni-1Y		X	X	X	X	X	X
Fe-25Cr-20Ni-1Pt	X			X	X	X	X
Fe-25Cr-20Ni-3Si		X	X	X	X	X	X
Fe-25Cr-6Al					X	X	X
Fe-25Cr-6Al-1Ce		X	X	X	X	X	X
Fe-25Cr-6Al-1Hf						X	X
Fe-25Cr-6Al-1La						X	X
Fe-25Cr-6Al-1Y		X	X	X	X	X	X
Fe-25Cr-6Al-1Pt		X	X	X	X	X	X
Fe-25Cr-6Al-3Si		X	X	X	X	X	X

1. Oxidation at 700°C in flowing oxygen.

2. Corrosion in $H_2/H_2O/H_2S/Ar$ at 700°C., $PO_2 = 10^{-20}$ atm.,
 and $PS_2 = 10^{-8}$ atm.

Oxidation and Corrosion Studies

The steady state oxidation kinetics of the alloys, Fe-25Cr-20Ni, Fe-25Cr-20Ni-1Hf and Fe-25Cr-20Ni-1Pt are parabolic under the test conditions reported here. (The pictorial weight gain vs. square root of time plot is not included in this report.) Alloys Fe-25Cr and Fe-25Cr-20Ni-1Pt did not exhibit any significant transient stage, and the oxidation was parabolic from the instant of initiation of oxidation reaction. Both developed scales of chromia, Cr_2O_3 as revealed by x-ray diffraction (XRD). Scales on Fe-25Cr-20Ni consisted of Cr_2O_3 and FeCr_2O_4 and these phases were determined by XRD. This scale on this alloy had distinct appearance along the substrate grain boundaries with Cr and oxygen, and the scales on the substrate grain interiors were rich in Cr and Fe^{2+} . The sizes of the chromia grains on Fe-25Cr at the oxide/gas interface varied between 0.2 and 2 μm .

The rate constants for mixed gas corrosion were determined assuming that corrosion kinetics were parabolic. Each data point in the weight gain vs. square-root-of-time plot was from a single coupon. Considerable scatter in the weight gain was observed for each alloy. The scatter is most likely to be due to variation in the extent of scale spallation during handling and the inherent sample-to-sample variation.

Table 2 gives the summary of rate constants for oxidation and oxidation/corrosion. The values for oxidation/corrosion are to be taken with reservation.

A variety of scale microstructure was observed in alloys so far studied, and specific patterns of scale degradation process were discernible. The degradation process seems to depend not only on the nature of protective oxide scales but on the elemental addition also in two of the three base alloys. Figures 1-22 are the representative scanning electron micrographs of scales that were observed on experimental alloys. In chromia forming Fe-25Cr alloy the scale breakdown occurred in the form of localized nodules appearing

Table 2 - Parabolic Rate Constant,
Kp g²/cm⁴ Sec.

Base Alloy	Additions, 1 Wt. %						
	NiL	Ce	Nf	La	Y	Pt	Si
Fe-25Cr	2.6x10 ⁻¹¹	*	9.6x10 ⁻¹²	7x10 ⁻¹³	6.9x10 ⁻¹³	3.1x10 ⁻¹¹	7.1x10 ⁻¹⁴
	1.8x10 ⁻¹⁴ (1)					≈10 ⁻¹⁴ (1)	
Fe-25Cr-20Ni	4.3x10 ⁻¹⁰	2.5x10 ⁻¹⁰	3.3x10 ⁻¹¹	2.6x10 ⁻¹¹	6.4x10 ⁻¹¹	1.8x10 ⁻¹⁰	6.3x10 ⁻¹⁴
	8.5x10 ⁻¹⁴ (1)		1.0x10 ⁻¹³ (1)			4.0x10 ⁻¹³ (1)	
Fe-25Cr-6Al	1.2x10 ⁻¹⁴	3.6x10 ⁻¹⁴	8.5x10 ⁻¹⁴	8.6x10 ⁻¹⁴	*	2.7x10 ⁻¹⁵	* -10 ⁻¹⁸

(1) Parabolic rate constant, Kp at 700°C in oxidation.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 1. SEM of scales on Fe-25Cr after 144 hours.

Figure 2. SEM of one of the nodules seen in Figure 1 at higher magnification.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 3. SEM of scales on Fe-25Cr-1Ce after 192 hours.

Figure 4. SEM of scales on Fe-25Cr-1Hf after 192 hours.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 5. SEM of nodule seen in Figure 4 at higher magnification.

Figure 6. SEM of scales on Fe-25Cr-1La after 144 hours.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 7. SEM of scales on Fe 25Cr-1Y after 144 hours.

Figure 8. SEM of nodule seen in Figure 7 at higher magnification.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ C$

Figure 9. SEM of scales on Fe 25Cr-1Pt after 144 hours.

Figure 10. Higher magnification SEM of corrosion scale seen at the sample edge in Figure 9.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 11. SEM of scales on Fe 25Cr-3Si after 144 hours.

Figure 12. SEM of scale flakes on Fe 25Cr-3Si after 144 hours.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ C$

Figure 13. SEM of scales on Fe-25Cr-20Ni-1Hf after 144 hours.

Figure 14. Magnified SEM of the oxide scale seen at the edge of the sample in Figure 13.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 15. SEM of scale at the gas/scale interface on Fe-25Cr-20Ni-1Hf after 144 hours.

Figure 16. SEM of scale seen below the porous scale, Figure 15 on Fe-25Cr-20Ni-1Hf after 144 hours.

Test Condition: $\text{PO}_2 = 10^{-20}$ atm., $\text{PS}_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 17. SEM of scale on Fe-25Cr-20Ni-3Si after 144 hours.

Figure 18. SEM of scale on Fe-25Cr-6Al after 144 hours.

Test Condition: $PO_2 = 10^{-20}$ atm., $PS_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 19. SEM of scale on Fe-25Cr-6Al-1Ce after 144 hours.

Figure 20. SEM of scale on Fe-25Cr-6Al-1Y after 192 hours.

Test Condition: $\text{PO}_2 = 10^{-20}$ atm., $\text{PS}_2 = 10^{-8}$ atm., $T = 700^\circ\text{C}$

Figure 21. SEM of scale on Fe-25Cr-6Al-1Pt after 192 hours.

Figure 22. SEM of scale on Fe 25Cr-6Al-3Si after 144 hours.

randomly on the surface, Figure 1. The nodule at higher magnification, Figure 2 consisted faceted corrosion products. This nodule contained Cr, S and Fe in the decreasing concentration levels suggesting sulfide of Cr and Fe. The effects of Ce, Hf, La, Y, Pt and Si on the formation of nodule and the breakdown of chromia scale are shown in Figures 3-12. In Fe-25Cr-1Ce, Cr was found in the scale shown in Figure 3. Sulfur was not found in the scale even after 192 hours. However, in other alloys of Fe-25Cr with ternary additions of Hf, La, Y, and Pt the nodules contained sulfides of Fe and Cr, Figures 4-10. The sulfidation was seen only near the edges in the case of Fe-25Cr-1Pt, Figures 9 and 10. A low weight gain was observed in Fe-25Cr-3Si even after 144 hours of exposure to oxidation/sulfidation. Only Cr was detected in the flakes and no sulfur was observed, Figures 11 and 12. The Fe-25Cr-20Ni and its derivatives with ternary addition of Ce, Hf, La, Y, and Pt exhibited similar breakdown process and scale morphology, Figures 13-16. These micrographs show scales observed on Fe-25Cr-20Ni-1Hf after 144 hours of exposure. The smooth scale seen at low magnification near the sample edge, Figure 13 is shown at higher magnification in Figure 14. The EDAX spectrum of this uniform scale suggests that it is chromia still in tact. Small white nodules seen randomly on the smooth chromia scale represent the initial stages of local scale breakdown by sulfides. When such nodules form closely and grow, they give an appearance of what is seen in the central region of the coupon, Figure 15. The gas/scale interface shown in Figure 15 is rich in Fe, Ni and S, suggesting sulfides of iron and nickel. Just below is seen faceted sulfides of Fe and Cr, Figure 16. The above three features are seen in all Fe-25Cr-20Ni-X alloys, except the silicon containing one. The effect of Si addition to Fe-25Cr-20Ni is shown in Figure 17, and the scale was essentially chromia not degraded by sulfur in 192 hours in contrast to the degradation reported in other Fe-25Cr-20Ni-X alloys. The corrosion behavior of Fe-25Cr-6Al-X alloys is different from that of Fe-25Cr-X and Fe-25Cr-20Ni-X where X = no. addition, Ce, Hf, La, Y, Pt or Si.

Three different types of behavior were seen in the case of Fe-25Cr-6Al-X, Figures 18-22. Grain boundary attack was prominent in Fe-25Cr-6Al-1Ce, Fe-25Cr-6Al-1La, Fe-25Cr-6Al-1Hf and Fe-25Cr-6Al-1Y. The reaction products in the grain boundaries of Fe-25Cr-6Al-1Ce, Figure 19, were rich in Fe and S, and the EDAX spectrum of the scale within a grain contained Fe, Cr and Al suggesting thin oxide scale and mostly contribution from the substrate. In Fe-25Cr-6Al-1Y grain boundary contained a high level of Al and Y and O, but the grain boundary particles were S-rich Fe, Al, Cr, Y compounds, Figure 20. Small white nodules were seen randomly on the surfaces of Fe-25Cr-6Al-1Pt and Fe-25Cr-6Al-3Si after 144 and 192 hours of exposure, Figures 21 and 22. These nodules were rich in Cr and O. The nature of oxide scale on Fe-25Cr-6Al-X alloys is yet to be confirmed, because the oxide is so thin that XRD and EDAX contain signals from the substrate.

It appears from the above observations that Fe enrichment occurs at the gas/scale interface in the chromia formers. How this transport leading to scale breakdown occurs remains to be established. The Fe-25Cr-20Ni and its derivatives exhibit fastest degradation process. Degradation is minimum in alumina formers. However, sulfidation seems to occur preferentially along the grain boundaries of Fe-25Cr-6Al-X where X = Ce, Hf, La and Y. These alloying additions segregate to grain boundaries because of their limited solubility. Si effects in all the three base alloys and Pt effect in Fe-25Cr-6Al differ from that of reactive elements addition.

Early Stages of Corrosion

The data collected from X-ray Photon Spectroscopy, (XPS), Auger Electron Spectroscopy and sputter depth profiling show a number of interesting observations. There is an increase in Fe concentration in the preformed oxide scales of Fe-25Cr and Fe-25Cr-6Al with the time of exposure to oxidation/sulfidation. This agrees with the SEM/EDAX observation of Fe enrichment at the chromia scale/gas

interface reported above. SIMS sputter profile of scales on Fe-25Cr-1Y shows lower concentrations of Y near the outer part of the scales for both the pre-oxidized and H₂S exposed conditions. Some discrepancies in the S concentrations were noticed, and they are being looked into.

Further work to understand the magnitude and the mechanisms of scale formation and breakdown will be conducted on selected alloys emphasizing the early stages of breakdown. The scales will be characterized by the surface analytical and TEM techniques. It is also planned to investigate the effect of a lower concentration (0.3 wt.%) of reactive elements added in bulk and incorporated by ion implantation.

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UND-3 - A STUDY OF EROSION PARTICLE REBOUND PARAMETERS

T.H. Kosel

Department of Materials Science and Engineering
University of Notre Dame
Notre Dame, IN 46556

INTRODUCTION

This research is designed to provide a systematic investigation of the effects of materials properties and experimental variables on the rebound directions and velocities of erodent particles. The general approach is to develop computer models for the impact of spherical and angular particles, and to compare the predictions with experimental measurements of both single and multiple impact rebound parameters. The project will also probe the question of the effects of various strengthening mechanisms on the dynamic flow stress of metals, which serves as the major material variable used as input for the computer rebound models. The project is primarily intended to develop computer models which can be used to predict the direction and velocity of rebound of a particle from a material, which is important in other programs aimed at computation of the flight path of particles through turbine engines. The rebound problem is also of interest from a purely scientific point of view, and because of the relationship between the energy lost and the amount of material removed by a particle during impact.

The computer models being developed will take into account several effects neglected in previous models, and will be used to concentrate primarily on the rebound problem. The project will include experiments in which rebound velocity measurements are made during both single and multiple-particle impact.

DISCUSSION OF CURRENT ACTIVITIES

Progress has been made in each area of the project, including the spherical and angular particle impact models, the velocimeter method, the single- and multiple-particle rebound experimental systems and dynamic hardness experiments. More work also remains to be done in each area. Work in the individual areas is described in the following sections.

Spherical Particle Impact Model

Significant effort has been spent on attempting to incorporate elastic wave energy losses into the spherical particle impact model, since it was found that such losses were necessary to explain the results for 90° impact.

The equations given by Hutchings for elastic wave losses are based on a paper by Hutchings,¹ who treated the normal impact of a sphere making a plastic indentation. His model assumed, as does our computer impact model, that the force resisting particle motion is just the product of the dynamic hardness and the area of contact. In order to find the energy lost due to elastic waves, he applied the results of an earlier paper by Hunter² which gave the total elastic wave loss as a function of the time dependence of the force on the sphere. With a slight approximation based on the assumption that the depth of the crater is much smaller than the radius of the sphere, he showed that this would lead to a sinusoidal variation of the force during loading. He also assumed a simple sinusoidal unloading force curve; the assumed force-time curve for the impact is shown in Figure 1. We note that in our computer model, we have verified that our force-time curve matches the loading portion of the curve in Hutchings' model rather closely for 90° impact. Our computer model does not explicitly calculate force as a function of time during rebound (unloading). The equations given by Hutchings for the fractional energy loss due to elastic waves were

Figure 1. Force-Time curve predicted for 90° impact of spheres according to Hutchings' model.¹ ω_p and ω_e are the frequencies of the sinusoidal loading and unloading portions of the curve.

based on one taken from Hunter's work² for the total energy loss W ;

$$W = KI$$

where K is a constant for a given material, which depends on Poisson's ratio and the density and longitudinal sound wave velocity for the material impacted. I is an integral over the Fourier components of the force-time curve;

$$I = \int_0^\infty \omega^2 |F(\omega)|^2 d\omega$$

Hutchings now introduced some additional parameters;

$$\alpha = 8I/F_0^2\omega_0,$$

where

$$\omega_0 = 2\omega_p/(1+e),$$

where e is the coefficient of restitution. F_0 is the maximum force exerted by the material on the sphere, which occurs at the instant it stops at the bottom of the impact crater. It is given by

$$F_0 = (4/3)\pi r^2 \rho v (3P/2\rho)^{1/2}$$

ω_p is the frequency which controls the loading portion of the force-time curve;

$$\omega_p = (1/r) (3P/2\rho)^{1/2}$$

where r is the sphere radius, P is the dynamic hardness of the material, and ρ is the density of the sphere. Since the value of the integral I depends on the shape of the force-time curve in Figure 1, we note that if we could change e independently of the material constants, the Hutchings analysis shows that only the unloading portion of the curve would change, according to

$$\omega_e = \omega_p/e.$$

It is difficult to physically picture how I would change for a change of e . We also note that e is in fact not independent of the loading portion of the curve, since P determines the loading curve and also the final area of contact, and the latter determines the stored elastic energy and therefore the rebound velocity and e .

It is important to note that F_0 is proportional to the incident velocity v , and that the Fourier components $F(\omega)$ are therefore also all proportional to v . Therefore, in the equation for α , the squared Fourier components inside the integral I are proportional to v^2 , and this exactly cancels the v^2 dependence of F_0^2 so that α is exactly independent of velocity v .

The fractional energy loss due to elastic waves is simply

$$\lambda = W/(mv^2/2).$$

Since W is proportional to the integral I and, as just noted, I is proportional to v^2 , it is important to note that λ is exactly independent of velocity.

Hutchings' final equation for λ was expressed in terms of α , material constants, and the coefficient of restitution e . However, as can be seen in the equation for W , e was not originally a part of the equations for the elastic wave energy loss, but rather it was introduced through the parameter α . The factor $\alpha/(1+e)$ appears in Hutchings' final expression for λ , and since $\alpha \propto 1/\omega_0 \propto (1+e)$, the final expression for λ actually depends on e only through the dependence of the Fourier integral I on the shape of the force-time curve.

Hutchings included a plot of α for the normal impact case to which his paper was devoted. However, we find that the equations in the paper

do not necessarily agree with the plot of α . The plot shows α decreasing very rapidly as e increases at first, whereas our Macintosh computer calculations using a Fourier transform algorithm from a textbook show that α usually increases at first. Since our calculation of α and λ in the spherical particle impact model requires a Fourier integral, we are checking to be certain whether there may actually be an error in Hutchings' plot of α . As described below, we are also comparing the results of our Macintosh Fourier routine with those obtained on our mainframe computer with a commercial Fourier routine. The point is critical, because if we use Hutchings' plot of α rather than our Fourier integral (which should be equivalent), we get very different results for the correction to the model due to elastic wave energy loss. If we use Hutchings' plot of α , the computer model produces quite good agreement with Hutchings' previously published experimental results for the impact of 9.5 mm diameter hardened steel spheres on mild steel. This was stated in our publication on the spherical particle model,³ in which we applied Hutchings' plot of α . However, if we use the Fourier integral, we get a much smaller reduction in the predicted rebound velocity.

We find that the numerical Fourier integration is subject to serious instabilities. We have written a separate program on our mainframe computer which simply computes the points on the force-time curve given by Hutchings, and computes α as a function of e using a commercially available Fourier analysis routine to evaluate the Fourier transform of the force-time curve. When we use a time interval of 2×10^{-7} sec for a total impact time of 10^{-5} sec (50 sampling points), α decreases rapidly with increasing e at first, and then becomes nearly constant, with the plot looking approximately like a hyperbola. This behavior is similar to that published by Hutchings. However, if we simply halve the time interval to 1×10^{-7} sec, α remains at a value very near zero and then increases rapidly for values of e over about 0.8. For longer time increments, the trend is similar to that for 2×10^{-7} sec, and for a shorter time increment it is similar to the one for 1×10^{-7} sec. These totally opposite trends of α with e depend entirely on the Fourier analysis routine, and point to a need to very carefully test this routine

to determine what the appropriate sampling time increment should be. It also appears that the routine applies a scaling factor to the Fourier components. We will be comparing results between the two Fourier packages to resolve this question, and testing them with functions for which we know the analytical Fourier components.

The model calculations to date have been based on the value of $P = 3.0$ GPa used by Hutchings as a best fit of his model to the experimental data. Since his model ignored stored elastic energy and therefore predicted a rebound velocity of zero at 90° , the fit of P to the data must have been made for low angles of incidence. We find that the change of rebound velocity with dynamic hardness predicted by the model (ignoring elastic waves) is much smaller for 30° incidence than for 90° incidence. Therefore, if we use a value of dynamic hardness calculated from the actual data of Hutchings for 90° impact, it does not cause as great a difference between the predicted and experimental values at 30° as we had before between the predicted and experimental values at 90° using the value of 3.0 GPa given by Hutchings. This is illustrated in Figure 2. However, the addition of elastic wave losses to the model should still be completed, since neither value of P gives good agreement for both 30° and 90° .

The spherical particle model has also been modified to plot the force on the particle as a function of time, to aid in evaluating the Fourier integral in the elastic wave analysis. We find that the sinusoidal shape assumed by the Hutchings model agrees closely with that computed by the model for normal impact, and thus does not affect the Fourier integral much. For impact at angles of incidence other than 90° , the spherical particle model uses the Fourier integral of the actual computed force-time curve to compute the elastic wave energy loss. For 90° incidence, or any angle near 90° for which the particle actually stops while still in contact with the material according to the model, the model computes the unloading portion of the curve according to the Hutchings assumption of sinusoidal unloading. For lower angles of

(a)

(b)

Figure 2. Comparison of the spherical particle model predictions with the experimental data of Hutchings for 30° and 90° incidence of 9.5 mm steel spheres on mild steel. a) $P = 3.0$ GPa, based on Hutchings best fit of the low angle data. b) $P = 0.55$ GPa, based on Hutchings' 47 m/s data.

incidence, the particle leaves the material without stopping, and no assumptions regarding the unloading curve are necessary.

The spherical particle model has also been revised to employ the Runge-Kutta method of integration, rather than the finite difference method employed in the original program, to see whether there would be any significant change in the results. The Runge-Kutta method gave very similar results for the computed rebound velocities and directions, but it gave noticeably different crater shapes. Since in some cases the crater shapes given by the Runge-Kutta method were slightly shorter in the direction of travel than they were wide, we believe there is some undetected problem with the code. Nevertheless, since quite good agreement was found for the rebound velocities and directions despite the differences of predicted crater shape, we feel that the accuracy of the original finite difference method is sufficient.

Angular Particle Impact Model

The angular particle model is being patterned after the existing finite difference method spherical particle impact model. For successive time increments, it will compute the forces on the particle based on the area of contact, assume constant translational and rotational velocities during the next time increment, and compute the increments of translational and rotational velocities during the time increment. At the end of the time increment it will evaluate the change of stored elastic energy based on the area of contact, and will adjust the velocity of the particle accordingly.

The particle will be assumed to be a flat plate of adjustable thickness, with a polygonal shape. The number of sides for the polygon, side lengths and angles will be adjustable by the program operator, as will be the initial assumed particle orientation and translational and rotational velocities. As many particle shapes will be considered as practical. The rebound velocities for one particular particle shape will vary depending on its initial orientation and rotational velocity, and this variation will depend on particle shape. The variation of rebound

velocity with shape and orientation will therefore be studied in addition to the variables of velocity and angle of incidence, and dynamic hardness. The mean of the rebound velocity distribution for several shapes and orientations will also be compared with the unique value from the spherical particle model for the same velocity and angle of incidence. The angular particle will be subject to large moments which will cause significant changes of rotational velocity, unlike the spherical particle model, in which it was shown that the relatively small moment on the particle caused little conversion of translational energy into rotational energy.

The appropriate technique for determining the area of contact in the angular particle model has been considered. Figure 3 illustrates an angular particle during the course of forming an impact crater. Since we expect a significant rotation of the particle during impact due to the

Figure 3. Schematic drawing of an angular particle impacting a planar surface. The center of gravity of the particle is indicated by a cross, and the new position and orientation of the particle after a short time increment is shown by the dotted line. The particle translates, and also rotates due to the large moment on it.

moment imposed on it by the force on the tip, a situation such as that illustrated will occur frequently. During a short time increment, the forward rolling motion of the particle due to the force on the tip has caused the portion of the rake face of the particle between points A and B to lose contact with the right side of the impact crater, while contact exists from B to C at the end of the increment. The model must therefore compute the point of intersection B between the rake face lines at the beginning and the end of the time increment, and use this to determine the new area of contact. This is also necessary for any other face for which an endpoint lies below the original flat surface. In the case shown, the rear face is not in contact before or after the particular time increment shown, but for a velocity vector more nearly normal to the surface it could be. The model must at each increment compute a polygon representing the shape of the impact crater created by the particle during the present and previous time increments.

Having determined the portions of the faces which are in contact with the material, the model will assign a force normal to each contacting face, at the center of the contact length, with a magnitude given by the product of the area of contact and the dynamic hardness. The effect of including a frictional force parallel to the face will also be evaluated; in the case illustrated, there would be a frictional force on the rake face of the particle, pointing down and to the left. The force system on the particle will then give the moment and body forces accelerating the particle during the next time increment.

The code for the model is partially completed now, and we expect it to be ready to run in the next few weeks.

Dynamic Hardness Apparatus and Results

The dynamic hardness apparatus is being used to measure the dynamic flow stress of metals by determining the energy lost by 635 μm diameter steel spheres during impact. The dynamic hardness can be calculated directly from the incident and rebound velocities, without measuring the crater dimensions, if we apply the theory given by Tabor.⁴ This offers a

significant advantage over other methods which have been used to calculate dynamic hardness based on the size of the impact crater, since measurement of the crater dimensions is both time-consuming and subject to errors of measurement and interpretation, as discussed below. However, before proceeding to application of the rebound dynamic hardness technique to the variation of dynamic hardness with strengthening mechanism, our first task is to compare the results from this method with those from methods based on measurement of crater dimensions. We are therefore measuring the crater dimensions after impact, as well as the rebound velocity, and different methods of calculating dynamic hardness are being compared. Dynamic hardness has been obtained for materials with different strengthening mechanisms (solution hardening, strain hardening, precipitation hardening, etc.).

The dynamic hardness apparatus is shown schematically in Figure 4. The particle is propelled through the flight tube into a vacuum chamber by compressed gas. As it enters the vacuum chamber, it passes through two light beams, rebounds from the target and passes through the light beams again. The diameter of the hole through which the particle passes in the detector block limits the range of rebound directions for which the rebound would be recorded, thus limiting the error possible from the assumption that the rebound angle is 90° . The parallel light beams used are 10 mm apart, and are generated by 9 watt quartz-halogen bulbs. A typical set of pulses from the photodiode detectors, after amplification by invert/filter/add operational amplifier circuits like that shown in the last report, is shown in Figure 5. The incident and rebound velocities are measured by two different counter-timers. The signal is prevented from passing to the rebound counter-timer until after the pulses have been generated by the particle on its way to the specimen. This is accomplished by triggering a flip-flop on the trailing edge of the pulse from the second light beam (closest to the specimen). The flip-flop controls a CD4066 bilateral analog switch which blocks the signal from entering the rebound counter-timer until the flip-flop is triggered. The amplifier and flip-flop circuits for the system are hardwired and contained in a single instrument enclosure.

Figure 4. Schematic drawing of the dynamic hardness test apparatus.

Figure 5. Typical set of pulses from the two light bams of the dynamic hardness test.

The specimen holder is cylindrical, and is mounted on a shaft which rotates in a vacuum feedthrough. By rotating the shaft between impacts, approximately 20 impacts can be made on the same circular specimen.

The compressed gas used to accelerate the particle is admitted into the gun tube by a solenoid valve which is pulsed by an MC555 timer integrated circuit, with its output buffered by a transistor. Earlier tests were done without the solenoid valve, by letting the chamber up to air, placing the particle in the outer end of the tube, sealing the end of the tube, evacuating the chamber, and unsealing the end of the tube. This resulted in a continuous inrush of room air which accelerated the particle. Concern with the question of whether the air stream was decelerating the particle during rebound led to addition of the solenoid valve.

Experimental results have been obtained for the dynamic hardness of 99.99% pure Cu as a function percent cold work, annealed 1100 Al, and 2024 and 6061 Al alloys in three different heat treated conditions. However, the results have generally given measured values of dynamic hardness which are lower than the measured Vickers static hardness values of the same materials. Rather than present and discuss the existing experimental results in terms of the effect of strengthening mechanism here, we therefore concentrate our attention on possible sources of experimental error which might lead to a lower dynamic than static hardness, which appears to contradict most other published data, and on the comparison of various methods of calculating dynamic hardness for our experiments.

We believe that the errors in measurement of the incident and rebound velocities are small, probably less than 1%. As discussed in the section on the velocimeter method, further (three-beam) tests are planned which will permit a quantitative experimental evaluation of the optoelectronic velocimeter error. Any errors present would be more or less self-canceling in any case since the same light beams are used for measurement of both the incident and rebound velocities. Also, the standard deviations of results are fairly small, 2 to 10% of the mean in terms of dynamic hardness values. However, there may be a systematic

error in the experiment if there is a source of energy loss other than plastic deformation of the specimen. One likely problem is deceleration of the rebounding particle by the intruding gas from the flight tube; this is discussed below. There appears to be no other significant source of systematic experimental error. No significant energy loss can be introduced by looseness in the mounting of the specimen holder, since simultaneous conservation of kinetic energy and momentum dictates a very small maximum energy transfer to the specimen because it is far more massive than the particles being used. For an elastic collision of a particle having a mass $1/1000$ that of an unsupported specimen, the kinetic energy transferred to the specimen is only 0.4% that of the kinetic energy of the rebounding particle. Our specimen holder is more than 1000 times as massive as the particle, so even with an unsupported specimen the energy transferred to it would be negligible.

An increase in rebound velocity was found for the solenoid valve results compared to the earlier method, as can be seen from the data in Table 1. We thus have reason to believe that there was some deceleration of the sphere by the intruding gas in the earlier experiments. However, since the values obtained for solenoid valve times of 24 and 73 ms are equal within the standard deviation of the results, it appears that the gas stream probably has little effect when the solenoid valve is used. More experiments will be done to try to verify this more conclusively.

We have done some experiments with a sabot carrying the sphere down the flight tube, since relatively little gas would be expected to escape past the sabot. However, this technique would need to be refined since the sabot introduced vibrations which affected the detector system, apparently through vibration of the lamp filaments. We have also tried pulling the flight tube farther away from the detector block to give the gas more room to expand and dissipate, but since the sphere does not travel perfectly straight from the end of the flight tube it rebounds through the light beams less frequently when this is done. It would be possible to replace the detector block with a pair of crossed flat laser beams, so that the gas could expand rather than being trapped in the hole in the detector block. It would also be possible to do rebound

experiments by dropping the spheres in front of a specimen attached to the end of the arm in our rotating arm erosion system. The rebound velocity would be measured by subtracting the specimen velocity from that measured in the lab frame of reference with a two-beam velocimeter.

Table 1.
Effect of Acceleration Method
on Dynamic Hardness Values of 6061-T6 Al

Method	Pressure (psi)	v (m/s)	Dynamic Hardness	
			Mean (MPa)	Std. Dev. (%)
Flowing room air	14.7	35	769	8.4
Solenoid valve, 73 ms	50	50	921	2.0
Solenoid valve, 24 ms	50		914	3.2
Solenoid valve, 22 ms	14.7	27	872	3.7
Air drop, 30 cm	-	2.4	708	10.1

A new experimental design of one of these types may be tried if ambiguities cannot be resolved by other means. However, the error introduced in the dynamic hardness value by the gas must in any case be small. This is because dynamic hardness is proportional to the energy lost by the sphere, which is given by

$$\begin{aligned}
 \Delta E &= 0.5m(v_i^2 - v_r^2) \\
 &= 0.5m(v_i^2 - e^2v_i^2) \\
 &= 0.5mv_i^2(1 - e^2),
 \end{aligned}$$

where e is the coefficient of restitution, defined as the velocity ratio v_r/v_i . ΔE would thus only vary between 0.84 and 0.96 of the incident energy if the coefficient of restitution varies between 0.40 and 0.20, a very substantial change of rebound velocity which we expect to be outside the range that could be introduced by deceleration due to intruding gas.

The dynamic hardness of the material, P , can be calculated by more than one method. Three methods are of interest. In the first, P is

given by E_0/V_C , where E_0 is the incident kinetic energy and V_C is the volume of the impact crater. This assumes that all the kinetic energy of the particle is dissipated in doing plastic work. Since we know that some of the initial kinetic energy is returned to the particle by elastic repulsion of the particle by the material after it comes to rest, the second method of calculating P which is of interest is to take it as $\Delta E/V_C$ where ΔE was given earlier and represents the energy lost by the particle during impact. A third method is to recognize that the rebound velocity is determined by equating the stored elastic energy in the material, at the instant the particle comes to rest at the bottom-most point of the impact crater, to the rebound kinetic energy. Thus, if we let the crater volume be determined by the incident kinetic energy and P , we can calculate the stored elastic energy, since this is a simple function of the crater radius which can be derived from Hertzian analysis.⁴ By equating the stored elastic energy to the rebound energy, we can derive the rather complicated equation given by Tabor⁴ for P as a function of only incident and rebound velocities. Since V_C is eliminated from the equation, it is not necessary to measure the crater dimensions for this method of calculating P , which we will refer to as Tabor's method. Table 2 gives results for P calculated by these three methods for one material, 6061-T6 aluminum.

Table 2.
Dynamic Hardness, P (MPa), for 6061-T6 Al by Three Methods,
Using Two Measures of Crater Radius
(22 ms solenoid gas pulse, 14.7 psi)

<u>Method</u>	<u>Using Inner Radius</u>	<u>Using Rim Radius</u>
E_0/V_C	1,420	1,100
$\Delta E/V_C$	1,380	990
Tabor	872	872
Static	1,150	1,150

The two different measures of the crater radius used in Table 2 were obtained from profilometer measurements of the crater cross sections. An

example of one of the profilometer traces is included in Figure 6. The inner radius is the radius at which the crater depth is equal to that of the surrounding flat (polished) surface, while the rim radius is that of the top of the raised rim of material which is pushed up by plastic deformation. The crater volume was calculated from the volume of a spherical cap with sphere radius equal to that of the incident particle, $317.5\text{ }\mu\text{m}$. This ignores the elastic relaxation of the crater during rebound, but since the elastic strain of metals at the yield point is only a few tenths of a percent this should produce negligible error.

When the rim radius is used, the values of dynamic hardness are all less than or equal to the static hardness, which was measured with a Vickers microhardness tester. (We plan to remeasure the static hardnesses of the materials using one of the same stainless steel spheres which are used for the impact tests as an indenter in our microhardness

Figure 6. Typical Profilometer trace of dynamic hardness impact crater.

tester. The load will be chosen to give a ratio of contact radius to sphere radius close to that obtained in the impact tests, in order to give the closest possible comparison between the impact and static hardness tests.) Using the inner radius does not affect the Tabor value of P since this does not require measuring the crater, but it does increase the other two measures of dynamic hardness quite significantly so that they are greater than the static hardness.

We believe that the appropriate measure of crater volume is that determined by means of the rim radius. Actually, the appropriate radius would be that where the crater profile first departs from the spherical surface, which would be somewhat inside the top of the rim; we will use this in the future. The slope of the rim of the crater is generally less than 20° , and the rim material between the inner radius and the point of departure from the sphere near the outer rim is actually in contact with the sphere. This rim material would be quite well supported even though it is slightly above the surface, and it should resist the advance of the sphere with very close to the same value of P as the material inside the inner radius.

It is interesting to note in this regard that the values of P obtained from E_0/V_C and $\Delta E/V_C$ agree better with that from Tabor's model⁴ if we use the rim radius than if we use the inner radius, although the agreement is not perfect in either case. The agreement is better for $\Delta E/V_C$ than for E_0/V_C , since Tabor's model also takes into account the energy carried away by the rebounding particle. We would consider perfect agreement of the Tabor and $\Delta E/V_C$ equations for P to be a verification of our experimental method for determining P based only on the rebound velocity, since the Tabor model is based on the same basic equation $PV_C = \Delta E$. The reasonable agreement of P values for the Tabor and $\Delta E/V_C$ models (13.5%) suggests that the rim radius is a more appropriate measure of crater volume than the inner radius. However, since there is still the possibility of an error due to deceleration of the particle by the intruding gas, we are not yet prepared to finish our evaluation of the technique.

Literature values of the ratio between dynamic and static hardness

range from one to over two, typically being higher than one. Our final analysis of the experiments will include a complete, critical review of other available experimental data. At the present, we do not feel that our data is in serious disagreement with published data, if the differences in technique for determining crater volume and for calculating P are taken into account. For instance, in one of the most systematic studies of dynamic impact hardness, Sundararajan and Shewmon⁵ found values of P ranging from 0.98 to 2.08 for eleven different alloys. These authors stated that they used optical microscopy to measure the crater dimensions, with the original target material surface as the reference point, and that they used the crater depth rather than its radius to calculate the crater volume. Since one would measure the depth of the crater by focusing on the flat surface and then on the bottom of the crater, this suggests that they may have used the inner radius as discussed here, which as we can see results in a significantly higher value of dynamic hardness. Also, they used E_0/V_c to obtain the dynamic hardness, rather than $\Delta E/V_c$, which would be expected to overestimate P due to ignoring the energy of the rebounding particle. If we could correct their dynamic-to-static hardness ratios to account for their use of the inner radius and neglect of rebound energy, their values would all be much closer to or less than one. Rickerby and Macmillan⁶ also used E_0/V_c to obtain the dynamic hardness, but we assume that they would have used the rim radius, since it is more readily measured by means of a microscope. For instance, Brinell hardness indentations are measured this way, and there would be no simple method of determining the inner radius. Finally, we note that the rebound velocity data of Hutchings⁷ for 9.5 mm steel spheres impinging on mild steel at 90° gives a value of P according to the Tabor model of only 0.4 GPa at 98 m/s, compared with his measured static hardness of 2.35 GPa.

Single-Particle Rebound Apparatus

The single-particle rebound experimental system is shown schematically in Figure 7. It is designed to provide data for comparison

(a)

(b)

Figure 7. Schematic drawing of the single-particle rebound experimental system. a) Two-dimensional simplified schematic. b) Three-dimensional schematic. S = specimen; L = laser diode; I = incident particle flight path; R = rebound flight path; D_x , D_y = detector pairs for x and y components of velocity; C = rotatable vacuum chamber with particle gun (not shown).

with computer calculations of the rebound velocity of spherical and angular erodent particles. Two pairs of 0.8 by 10 mm cross-section laser light beams are employed to measure the incident and rebound velocities. This application of the velocimeter method differs from most others in that it is necessary to have long light beams. One pair of beams is parallel to the specimen surface and just above it, and the other is perpendicular to the surface and nearly touching the specimen at the side adjacent to which the particle strikes. The time of flight between the beams parallel to the surface will give the y component of rebound velocity (in the direction perpendicular to the surface) and the other pair of beams will give the x component of rebound velocity. From these we can calculate the direction and the magnitude of the total rebound velocity vector. Since we know the preset the angle of incidence, we can compute the incident velocity from the y velocity component as the particle approaches the specimen. Three counter-timers are needed for this experiment. A flip-flop switching circuit is used as described above for the dynamic hardness apparatus, to prevent the incident pulses from reaching the y-component rebound velocity counter-timer. The light beam system employs a 20 mW infrared laser diode as a light source, with a gradient index lens to collimate the beam. The beam is spread into an 0.8 by 10 mm cross section by a pair of cylindrical lenses, split into a pair of parallel beams by a beam-splitter and mirror combination, and then the two beams are split again and routed appropriately by mirrors. Light beams are indicated by dashed lines in the two-dimensional sketch and by solid lines in the three-dimensional sketch. Beam-defining slits are placed in front of the detectors.

The single-particle gun used with this system is to be the same as that already in use with the dynamic hardness system, with a solenoid operated valve switched by a single pulse providing a gas pulse which accelerates the particle. The gun is to be mounted parallel to the base plate, through a hole in the side of the cylindrical vacuum chamber. The chamber rests on an O-ring, and can be rotated to a new angle of incidence by bringing the system up to air. The large bracket over the top of the chamber is used to provide a rotation axis for the chamber and

particle gun, which must point accurately at a point near the edge of the specimen. At each angle of incidence, several single-particle impacts will be made along the edge of the specimen, which will be mounted on a stage which moves the specimen vertically via a mechanical vacuum feedthrough in the base plate.

The cylindrical lens arrangement and the laser diode were both tested experimentally before proceeding with the rest of the design. A special power supply was designed for the laser diode, since it is necessary to have a very stable light intensity with no noise level which might be transmitted to the photodiode detectors. The power supply employs a battery-driven Zener diode to provide a very clean dc voltage, and this is buffered by an operational amplifier driving a transistor output stage. A hardwired electronic system which includes the amplifiers and flip-flop switching circuits for the four light beams, and the laser diode power supply, has been constructed.

The machine shop work on the single-particle rebound apparatus is nearly complete. Delivery of the parts is expected by October 31, and it is hoped that assembly, alignment and testing of the system will proceed quickly.

Optoelectronic Velocimeter

Work on the optoelectronic velocimeter method since the last report has included additional velocity calibration with a greater light beam spacing, improvements in the light source to improve pulse sizes, isolation of two sources of extraneous pulses being produced in the rotating arm erosion system, planning of a new experiment to permit quantitative evaluation of the accuracy of the method, and revision of the amplifier system.

Calibration with 10 mm Leading Edge Spacing

A calibration curve for the mean of velocity distributions from the rotating arm system against the rotor tip speed was shown in the last report for 138 μm crushed quartz particles with a leading edge spacing of

3.0 mm for the light beams. The slope and intercept were 0.9625 and 0.061 m/s respectively, and the correlation coefficient was 1.000. As shown in Figure 8, a similar calibration resulted from new data taken with a 10 mm leading edge spacing, with slope and intercept values of 0.9861 and 0.51 m/s respectively. The velocity measurement thus gives an excellent measure of the true velocity. The fact that the slope values are not exactly one is apparently due to the observed fact that the velocity distribution changes a little with velocity, becoming slightly wider at higher velocities.

The main purpose of the experiment with a 10 mm spacing was to be certain whether part of the width of the velocity distribution observed with smaller spacings might be due to time measurement errors between the

Figure 8. Calibration of optoelectronic velocimeter against tip speed of rotor in rotating arm erosion system for 138 µm crushed quartz particles with a 10 mm leading edge spacing for the light beams.

leading edges of the pulses. Most timing errors, such as distortion of pulse shape or time delays due to the amplifier would be nearly self-canceling in the two-beam method, since the amplifiers for the two channels are identically constructed. The chief error is expected to arise from a difference in the actual shapes of the light pulses from the two beams, due to rotation of the particle as it passes between the beams. Since we are primarily interested in angular particles, any such rotation would give rise to a change in the cross-sectional area presented to the light beam, and a possible small change in the amount of transmitted light. (We observe that most particles are actually fairly opaque, even for quartz or alumina particles.) Since the time at the leading edge of the pulse is measured at a trigger level somewhat displaced from the baseline (usually by about 10%), if the slopes of the leading edges of the two pulses differ there will be a different offset of the trigger point from the true leading edge of the pulse. We refer to this as a slope error. For a given slope error, the fractional error in the time of flight between the two beams increases as the leading edge spacing decreases.

Figure 9 shows velocity distributions taken in the rotating arm system with 138 μm crushed quartz particles for leading edge spacings of 0.8, 3.0 and 10.0 mm. The width of the distribution is slightly less for a leading edge spacing of 3.0 mm (9b) than for 0.8 mm (9c), but the distributions are fairly symmetrical. In contrast, the distribution in Figure 9c for a 10.0 mm spacing shows two distinct peaks. The standard deviations of the distributions are 9.3, 8.8 and 9.1% respectively. The similarity of the standard deviations suggests that any slope errors must not be very significant, since there is no very significant narrowing of the distribution for larger leading edge spacings. However, the double peak of the distribution found with 10.0 mm spacing is apparently not due to statistical problems, since another distribution obtained from 10,000 particles instead of the 1,000 in Figure 9c was similar. We do not believe that the lower velocity peak is due to aperture deflection losses, because with a 10 mm spacing the fraction of particles striking

Figure 9. Velocity distributions from the rotating arm erosion system for 138 μm crushed quartz particles. a) No spacer in crossed-beam configuration; leading edge spacing 0.8 mm. b) Leading edge spacing 3.0 mm, crossed beam. c) Parallel beams, leading edge spacing 10.0 mm.

the aperture just in front of the first beam, being deflected through a large enough angle to have significant energy loss, and still passing through the second beam must be very small. However, there is some question as to whether the shape of the apparently bimodal velocity distribution is masked by measurement errors such as slope errors in the two distributions with smaller leading edge spacings. We will return to this question shortly. It should be mentioned that the velocity distributions are wider than had been expected for the rotating arm system, and the reason for the relatively wide distribution is not well understood. We believe that it is partly due to particles which convert some of their translational energy to rotational energy by rolling as they exit the slots in the end caps on the ends of the rotor.

The exact precision of the velocity measurement has not yet been determined as conclusively as desired, because the magnitude of the slope errors believed responsible for any lack of precision is difficult to evaluate. We can put an upper bound on the slope errors if we assume a reasonable approximation to the pulse shape and estimate the time offset from the true beginning of the pulse to the trigger level. If we trigger at 25% of the pulse size, which is a much higher than the 10% we actually typically use, the trigger level offset would be roughly 12.5% of the pulse width, assuming a triangular shaped pulse. If the pulse at the second beam were perfectly square instead of triangular, and there were no spacer block, then we would have a 12.5% velocity error due to this extreme difference of slopes. If the spacing were 10.0 mm instead of the 0.8 mm with no spacer, the error would only be 1.25% even due to such an extreme assumption of the possible difference of slopes. Since the pulses from both channels are always very similar in shape, this is a severe overestimate of the slope error. This implies that we should expect the errors for 10.0 mm spacing to be less than 1%. Since the standard deviations of the velocity distributions with 10.0 and 0.8 mm spacings are similar, any broadening of the distribution by measurement errors must be fairly small. However, it is still not clear whether the bimodal velocity distribution for 10.0 mm spacing may be masked by measurement errors for the smaller leading edge spacings.

To try to evaluate the slope error, we discussed in our last report an experiment in which we collected the digital oscilloscope pulse shapes for 100 pulses and had the computer determine how much the velocity measurement differed for a trigger level immediately adjacent to the baseline (50 mV) compared to one at a more realistic level (350 mV). The velocity was calculated for each trigger level, and the ratios of the velocities was taken. The experiment was done with 138 μm crushed quartz particles and a leading edge spacing of 3.0 mm. The standard deviation of the ratios was only 0.89%, which shows that the slope errors were quite negligible. Assuming the same slope error would occur for each particle even with no spacer (0.8 mm leading edge spacing), we found the standard deviation would be expected to be 3.3%, still not very large. Thus, we believe that the slope error problem is negligible for a 3.0 mm spacing, and small for 0.8 mm. Still, it would be better to have a better method of quantitatively measuring the inherent accuracy of the technique, since we are not certain of the source of the bimodal velocity distribution in Figure 9c.

Three-Beam Experiments

To resolve the question of the true accuracy of the method, we plan to conduct an experiment using three light beams. One counter-timer will measure the velocity based on the time between beams 1 and 2, and another will measure the time between leading edges for beams 2 and 3 for the same particle. A second computer-interfaced counter-timer is on order for this purpose, and for use in the multiple-particle rebound experiments. The ratio of the two measured velocities for the particle will then be taken, and the distribution of these ratios will be examined. If there were no error, the ratio would be exactly one, so the ratio will give the percentage error directly on a particle-by-particle basis. This method has the advantage that it is unnecessary to make any assumptions as to the source of any deviation of the ratio from 1.0; it will give the repeatability of the measurement for single particles unambiguously. While we are convinced that the method is highly accurate, this experiment will allow us to state the accuracy with more

precision. The three-beam experiments can be done first with equal 10 mm spacings between the beams to evaluate the precision of the method at this spacing. We expect this precision to be of the order of 1%. Then, we can repeat the experiment using two crossed beams with no spacer block, with a leading edge spacing of 0.8 mm, and the third beam at a spacing of 10 mm. This will allow evaluation of the precision of the crossed-beam method for use in denser particle flows such as gas-jet erosion systems.

Another experiment which will be possible with the additional computer-interfaced counter-timer is to obtain the ratio of velocities measured via both the two-beam method with a 10 mm leading edge spacing, and the single-beam method. This ratio would be done for each particle, which was not possible with a single computer-interfaced counter timer. This experiment would allow evaluation of the precision of the single-beam method, which has the advantage for some situations that it is not necessary to have an aperture with attendant deflection losses.

Light Source Improvements

Nearly all experiments to date have used a 9 watt quartz-halogen lamp as a light source, mounted nearly in contact with the crossed-beam block. This has given adequate pulse sizes, about 2 V for 138 μm crushed quartz particles. However, it is desirable to increase the light intensity further in order to be able to work with smaller particles, especially since the much larger number of ps per second with a smaller particle size at a constant mass feed rate will be a significant advantage in the multiple-particle rebound experiments. Also, the proximity of the quartz-halogen lamps to the aluminum crossed-beam block causes the block and the photodiodes to be extremely hot during operation, not enough to degrade performance but enough to affect lifetime. We therefore considered other light sources. Since we know that pulse size ΔV is proportional to $i_0 R$, where i_0 is the current through the photodiode and R is the resistance in series with it, and since i_0 is directly proportional to light intensity, we used the voltage drop $i_0 R$ across the photodiode series resistor as a measure of the light source intensity.

The value of i_0 with the 9 watt quartz-halogen lamps with the crossed-beam block, which has 800 by 1000 μm light beam channels and a source-to-detector distance of about 20 mm, was 0.3 mA. With a 2 mW helium-neon laser, we obtained a value of 1 mA, and with a 20 mW laser diode we obtained 6 mA. Since both these values were obtained with no slits, i_0 would decrease with addition of a slit. Both types of laser produce parallel illumination, so that the distance between the source and detector is not a consideration as for the quartz-halogen bulb. (A gradient-index lens is used with the laser diode to give a parallel beam.) The helium-neon laser is a relatively bulky source, and the laser diode is a rather expensive type of source; but both have the advantages that they do not heat the detector as does the quartz-halogen lamp and that they are more intense.

Experiments with a 300 watt quartz-halogen slide projector lamp, which produces a rough focus about 2 cm in diameter, show that even with the large intensity loss introduced by a bifurcated 3mm diameter fiber optic cable, we can obtain a light current of 8 mA through a hole having the same area as our 800 μm by 1000 μm crossed-beam block slit. This is about 27 times more light intensity than with the previous slit block arrangement. This is partly due to the reduction of the distance between the photodiode and the light source (the end of the fiber optic cable) to about 5 mm; this would not be possible with the small lamp due to extreme heating of the photodiode.

Since the pulse size is proportional to i_0 , the increase in light intensity will allow us to detect smaller particles, which means that for a constant mass feed rate we will detect more particles per second and improve the throughput of the multiple-particle impact experiments. Another advantage of the higher intensity is that for a given particle size we will have much larger pulses, so that we should be able to trigger at a level which is a much smaller fraction of the pulse height. This should improve the precision of the measurement. In addition, the fiber optic cable does not have to be nearly as carefully aligned as the quartz-halogen lamp, and two beams of equal intensity are obtained from the bifurcated fiber optic cable. Thus, this light system offers several

significant advantages over others in addition to being inexpensive, and it is therefore incorporated in the design of the experimental system for multiple-particle rebound studies. It would also be an excellent light source for gas-jet incident particle velocimetry.

AC Coupled Amplifier

It is somewhat simpler to use an ac coupled op-amp circuit such as that shown in Figure 10. The capacitor C at the positive input to the op-amp forms a high-pass filter with R, with a time constant RC. The ratio of the filtered signal level E_f at the op-amp input to the level E_{pd} coming from the photodiode is given by

$$E_f/E_{pd} = 1/[1 + (\omega/\omega_0)^2]^{1/2},$$

where ω is the input frequency and $\omega_0 = 1/RC$ is the cutoff frequency defined by the time constant RC. The input filter eliminates the dc component of the input signal, which is desirable since it forces the signal level at the op-amp input to be inside the op-amp power supply voltage range. It also eliminates any slow drift of the baseline

Figure 10. Schematic drawing of an ac coupled op-amp circuit to replace the earlier invert/filter/add circuit. A second stage can be added to increase the gain.

voltage. In addition, the time constant can be adjusted to discriminate against any possible long pulses. For instance, the long pulses generated by particles striking the wires inside the rotating arm erosion system would be at least partially screened out, although we expect to eliminate this effect by shielding the wires. With the more intense light source we will be using in the multiple-particle rebound experiments, it is also desirable to use the ac coupled circuit because the dc level of the voltage across the resistor in series with the photodiode in the input circuit need not be inside the op-amp power supply range.

Causes of Extraneous Pulses

A minor experimental problem is that a small percentage of the particles tends to deflect into the light beam channels in the crossed-beam block. In addition to a gradual blocking of the light beam by particles which come to rest in the channels, this creates superfluous very long pulses. This has been solved by enlarging the hole through which the particles pass except for the end into which they enter, and by lining the hole with a replacable glass tube. This is found to eliminate many but not all of the extraneous very slow pulses we had observed during calibrations in the rotating arm erosion system.

Another minor problem has been that some extraneous very broad pulses are produced which only occur when the particle feeder is turned on. These are not due to electronic noise from the feeder motor, since they do not occur if the feeder is on but empty; they must therefore be due to the particles themselves. Since these pulses still occur when the entrance hole to the light beam area is blocked, but the light beams are on so that all conditions are otherwise normal, we believe that the extra pulses are produced by particles striking the wires inside the rotating arm vacuum chamber, and that it will be solved by rerouting all wiring inside protective tubing.

Multiple-Particle Rebound Apparatus Design

The multiple-particle rebound system is designed to operate inside our rotating arm erosion system. Since this system operates in vacuum, there will be no question concerning deflection of the particles by air streams. The apparatus includes a crossed-beam incident velocimeter to measure the velocity of each incident particle, since the velocity distribution in the rotating arm system is broader than had been realized before the development of the velocimeter (Figure 9).

Figure 11 shows a simplified schematic drawing illustrating the two motions of the crossed-beam rebound velocimeter, each of which will be driven by a separate stepping motor controlled by the computer, which will also move the specimen, control the counter-timers for the velocimeters and collect the velocity data. For a given angle of incidence, the computer will move the rebound crossed-beam velocimeter to successive rebound angles, measuring the rebound particle velocity distribution and the count rate at each rebound angle. The rebound

Figure 11. Schematic illustration of the rebound particle detection geometry.

detector will also be able to move sideways out of the the plane of incidence (defined by the specimen surface normal and the incident direction), under the control of another stepping motor. This will allow determination of the velocity distribution and particle flux out of the plane of incidence. The four light sources needed for the two crossed-beam velocimeters will be derived from two bifurcated fiber optic cables illuminated through a port by a single 300 watt slide projector lamp mounted outside the vacuum chamber.

Figures 12a and 12b, respectively, show schematic top and side views of the apparatus, which will be mounted inside the rotating arm erosion system. The particles will first pass through a stationary incident velocimeter which is not shown. The hole in this velocimeter will define a small impact area on the specimen, and the axis of the hole of the rebound velocimeter will always be pointed at the center of the impact area on the specimen. The incident particle stream is horizontal in the rotating arm system, and to change the angle of incidence the specimen will rotate about the vertical z axis. The stepping motor C which will accomplish this motion is not shown, but will be mounted to one side in the side view drawing, on the base plate of the vacuum chamber. This motor will drive a chain drive pulley on the vertical specimen axis shaft. The motion of the rebound velocimeter about the point of impact is to be accomplished by motor A, seen in the side view, which is mounted to the base plate of the vacuum chamber. The shaft of this motor is fixed to a T-shaped block by means of a hollow shaft into which the vertical specimen shaft fits coaxially. The T block holds the axis of the shaft upon which the rebound velocimeter will be mounted on the end of an L-shaped bracket. The L bracket is operated by motor B which is mounted on the T block as seen in the top view, by means of a chain drive pulley (not shown).

Normally, to simply scan through different rebound angles, motor A will change the detector position, with the L bracket horizontal so that the detector lies in the plane of incidence. To change the specimen position and angle of incidence, motor C will be actuated. For experiments in which we wish to study the scattering out of the plane of

Figure 12. Schematic illustration of the multiple-particle rebound detector apparatus. (a) Top View. (b) Side View.

incidence, we will use motor B to move the L bracket to different angles out of the plane of incidence, holding the rebound and incident angles the same.

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UTN-3 - AQUEOUS CORROSION OF IRON ALUMINIDES

R. A. Buchanan and J. G. Kim

Department of Materials Science and Engineering
The University of Tennessee
Knoxville, Tennessee 37996

INTRODUCTION

A current research program at the Oak Ridge National Laboratory (ORNL) involves development of low-cost intermetallic alloys based on Fe₃Al with optimum combinations of strength, ductility, and corrosion resistance for use in advanced fossil energy conversion systems. Much of this effort has involved alloying-element additions to compositions near Fe₃Al for improvements in room-temperature ductility (from a base of only 1-2%) and hot strength above 600°C.¹ It is the purpose of the project herein described to study the aqueous corrosion characteristics of these experimental iron aluminides. This report summarizes a nine-month effort, which has primarily entailed generation and analyses of cyclic anodic polarization curves in acid, neutral-chloride, and basic solutions. The effort has also involved determinations of average corrosion rates in selected systems by two electrochemical methods: Tafel extrapolation of cathodic polarization curves, and the use of small-potential sweeps through the corrosion potential with subsequent statistical analyses. Future evaluations will involve selected mass-loss immersion tests.

DISCUSSION OF CURRENT ACTIVITIES

Initially in the project, the objectives involved corrosion characterizations of four iron-aluminide compositions and one nickel-iron aluminide. All materials were fabricated at ORNL. The nominal compositions of the iron aluminides were Fe-28 atomic percent Al plus 0, 2, 4, and 6 atomic percent Cr, with designations of FA-61, FA-77B, FA-72C, and FA-78, respectively. These alloys were evaluated in both

air-annealed (1 h at 850°C plus 5d at 500°C) and 10% cold-worked conditions. The nickel-iron aluminide (70.66% Ni, 11.2% Fe, 9.54% Al, 6.95% Cr, 0.35% Zr, 1.28% Mo, 0.02% B), designated as alloy 357, was evaluated in the vacuum-annealed condition only (1h at 1100 °C). Later, as the project evolved, two additional iron-aluminide compositions were added: Fe-28 atomic percent Al, plus 2 atomic percent Cr, plus 1 and 2 atomic percent Mo, with designations of FA-86 and FA-85, respectively. These materials were evaluated in the air-annealed condition only (1 h at 850°C plus 2d at 500°C).

Samples were prepared for electrochemical testing in the following manner. An electrical connection was made to each specimen by means of a soldered brass screw on the back sample surface. The sample was then mounted in Maraglas 655 epoxy, and the front sample surface was uniformly exposed by wet grinding with 600 grit SiC paper. The metal/epoxy interface was coated with Glyptal 1201 Red Enamel to minimize problems with interface crevice corrosion. The exposed metal surface was again ground with 600 grit SiC paper to remove air-formed oxide films immediately before attachment of the mounted sample to a glass-insulated sample holder and immersion into the electrolyte of the polarization cell.

The program initially involved anodic polarization testing at ambient laboratory temperature in four electrolytes over a wide pH range: 1N HCl (pH~0.5), 1N H₂SO₄ (pH~0.5), 3.5% NaCl (pH = 7), and 1 N NaOH (pH~14). This selection of electrolytes also provided indications of the effects of chlorides on corrosion behavior. The electrolytes were continuously saturated with oxygen before and during polarization testing. Each cyclic anodic polarization test consisted of first allowing the steady-state open-circuit corrosion potential to be established (< 1 mV change per minute), then scanning the potential in the anodic direction at a rate of 600 mV/h while measuring the current density. The scanning direction was reversed to complete the cyclic curve at a terminating current density of 10^{-3} A/cm². The results for the initial four iron aluminides (0,2,4, and 6% Cr) and the nickel-iron aluminide are summarized in the following sections.

1N Hydrochloric Acid. This strong hydrochloric acid solution was very aggressive toward the iron aluminides and the nickel-iron aluminide. Only active behavior, i.e. continuously increasing current density with increasing potential, was demonstrated for all materials in all conditions. Examples of this behavior are shown in Figures 1 and 2.

1N Sulfuric Acid. During the initial series of tests on the iron aluminides, the potential scan direction was reversed at 10^{-1} A/cm² after only active behavior was demonstrated in this strong sulfuric acid solution. Subsequent tests indicated that passivation does occur at higher potentials after a critical anodic current density equal to or greater than 10^{-1} A/cm² is exceeded. An example is shown in Figure 1. Nevertheless, the corrosion potential for all the iron aluminides in both annealed and cold-worked conditions existed within the active range. The nickel-iron aluminide demonstrated better behavior with a maximum active current density of 10^{-3} A/cm² and a passive current density of 10^{-4} A/cm².

Figure 1. Typical Cyclic Anodic Polarization Behavior of Iron Aluminides

3.5% NaCl, pH = 7. All materials exhibited passive behavior with hysteresis in the neutral 3.5% NaCl solution, indicating susceptibility to localized pitting/crevice corrosion. For all of the iron aluminides in both conditions, the protection potential was below the open-circuit corrosion potential, indicating that localized corrosion could occur during the freely-corroding condition. An example is shown in Figure 1. For the nickel-iron aluminide, the protection potential was above the open-circuit corrosion potential (Figure 2), indicating a higher degree of resistance to crevice/pitting corrosion.

Figure 2. Cyclic Anodic Polarization Behavior of Nickel-Iron Aluminide

1N Sodium Hydroxide. All materials in all conditions exhibited ideal passive behavior in this very basic solution. Passive current densities were in the 10^{-5} - 10^{-6} A/cm² range. Breakdown potentials were quite high, and no hysteresis was exhibited indicating excellent resistance to localized corrosion. An example is shown in Figure 1.

Selected combinations of materials and electrolytes were subjected to electrochemical tests to evaluate corrosion rates under freely-corroding conditions as an additional means to confirm the trends indicated by the above anodic polarization results. Corrosion rates for the 0% Cr and 6% Cr iron aluminides, and the nickel-iron aluminide, were evaluated in 1N H₂SO₄ and 3.5% NaCl solutions. Two methods were employed. The first method involved Tafel extrapolation of cathodic polarization curves to determine corrosion current densities. This method proved difficult in certain cases, however, due to complications arising from nonlinearities in the cathodic curves in the aerated acid solution. Consequently, a second method, judged to be more accurate, was also employed. This method involved small-potential sweeps through the corrosion potential (± 25 mV) with subsequent statistical analyses. Using the Butler-Volmer model, linear regression was used to obtain first approximations to the Tafel slopes, then nonlinear regression was employed to determine the Tafel slopes and corrosion current density which best fit the experimental data. Once the corrosion current densities were determined by each method, Faraday's law was used to calculate average corrosion penetration rates in mils per year (mpy). Results are presented in Table 1. These results were consistent with indications derived from the polarization behavior of the iron aluminides, that is, relative high corrosion rates in the strong acids, low average rates in neutral chloride solution (but definite susceptibility to localized corrosion), low rates in the basic solution, and little differentiation of Cr alloying effects.

Based on the above results, and relative to the iron aluminides, it was tentatively concluded that the four electrolytes were either too aggressive (1N HCl, 1N H₂SO₄, and 3.5% NaCl (with respect to localized corrosion)) or insufficiently aggressive (1N NaOH) to allow differentiation of the Cr alloying effects. Consequently, a fifth electrolyte was designed to simulate an aggressive acid-rain-type atmospheric-corrosion situation. This electrolyte consisted of an aqueous solution containing 200 ppm Cl⁻ and at pH = 4 (H₂SO₄). Cyclic anodic polarization and immersion tests were conducted in this solution.

Table 1. Results of Electrochemical Evaluations of Corrosion Penetration Rates

Material	Average Penetration Rate (mpy)			
	1N H ₂ SO ₄		3.5% NaCl	
	Tafel Extrapolation	Statistical Method	Tafel Extrapolation	Statistical Method
Fe-28a/o Al (Cold-Worked)	546	1,464	6.3	5
Fe-28 a/o Al + 6 a/o Cr (Cold-Worked)	618	524	1.03	0.07
Nickel-Iron Aluminide (Annealed)	236	34	0.59	0.16

200 ppm chloride, pH = 4. In this solution, the anodic polarization behavior of the nickel-iron aluminide improved relative to the 3.5% NaCl solution by demonstrating higher breakdown and protection potentials (Figure 2), as expected because of the reduced chloride concentration. For the iron aluminides (Figure 3), again, the protection potentials were below the corrosion potentials. However, the breakdown potential increased with Cr content, indicating increased relative resistance to initiation of localized corrosion. Samples of each annealed material were immersed in this solution and observed over a three-week period. After one day, orange-brown corrosion products were seen at crevice locations on the Fe₃Al + 0% Cr material. After two days, similar deposits were noted at edge locations on the Fe₃Al + 2% Cr sample. The other samples (Fe₃Al + 4% Cr, Fe₃Al + 6% Cr, and nickel-iron aluminide) remained visually clean for the entire three-week period.

To provide a frame of reference for comparison, the anodic polarization curves of Types 304L and 316L stainless steel were also determined in the 200 ppm Cl⁻, pH=4, electrolyte. These curves along with those of the nickel-iron aluminide and the 6% Cr iron aluminide are

Figure 3. Cyclic Anodic Polarization Behavior of Iron Aluminides in Aqueous Solution Containing 200 ppm Cl^- at $\text{pH} = 4$.

compared in Figure 4. It is seen that the major problem associated with the 6% Cr iron aluminide is its low protection potential.

At this point in the evolution of the project, it became of interest to examine the effects of Mo on the anodic polarization behavior of the iron aluminides containing Cr. For this purpose, ORNL supplied two additional vacuum-annealed alloys, both containing 2% Cr, one containing 1% Mo, the other 2% Mo. The anodic polarization curves for these additional materials, along with that of the 2% Cr iron aluminide containing no Mo, are shown in Figure 5. It is apparent from these data that Mo additions raise the protection potential -- an important result in terms of increasing the resistance of iron aluminides to localized, chloride-induced, aqueous corrosion.

Figure 4. Cyclic Anodic Polarization Behavior of Stainless Steels, Nickel-Iron Aluminide, and Iron Aluminide (6% Cr)

Figure 5. Effects of Mo on the Cyclic Anodic Polarization Behavior of 2% Cr Iron Aluminide

In view of the overall results, it would be of considerable interest to evaluate the aqueous corrosion characteristics of iron aluminides containing 4-6%Cr and also containing Mo at concentrations up to approximately 2%.

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VPI-3 - ALKALI ATTACK OF COAL GASIFIER REFRACTORY LININGS

J. J. Brown

Department of Materials Engineering
 Virginia Polytechnic Institute and State University
 Blackburg, Virginia 24061

INTRODUCTION

This investigation was initiated in 1985 in an attempt to understand the effect of alkali species on the corrosion of coal gasifier refractories. The alkali-refractory corrosion in non-slagging coal gasifiers and in the non-slagging portions of slagging gasifiers was examined. The alkali species in a typical gasifier atmosphere were calculated using the SOLGASMIX-PV computer program. Reactions between alkali and refractory castables, fireclay refractories, and alumina-chromia brick were first computed theoretically and then selectively confirmed experimentally. Alkali-alumino silicate compounds were synthesized and their thermal expansion properties and water solubilities were measured.

Below 20 atm pressure, alkali is present in gasifiers as solid or liquid oxides, hydroxides, carbonates, or sulfides up to about 1400K; above this temperature most of the compounds exist as vapor species, including alkali metal vapor. At 1400K and above, the specific alkali phases are quite pressure sensitive.

Alkali corrosion of calcium aluminate castable refractories is primarily confined to the cement phase. The most common reaction products include sodium aluminate ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$), $\text{Na}_2\text{C}_3\text{A}_5$ ($2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$), nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), potassium aluminate ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$), and kaliophilite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). All of these compounds were found to have high thermal expansion coefficients and significant solubility in water. Of the compounds tested, the

formation of potassium aluminate would be the most detrimental to the gasifier lining. The linear thermal expansion of potassium aluminate was 2.05% from room temperature to 800°C, which was twice as large as the other compounds. Potassium aluminate also possessed the highest solubility in water which was 8.89g/L at 90°C.

The results of alkali corrosion of alumina/chrome refractories, both experimental and theoretical, show formation of alkali-aluminate ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$) and β -alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, $\text{K}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$) compounds with formation of several metastable alkali compounds. Sulfur did not appear to affect the reaction products. Alkali distribution into the alumina-chrome refractory is rapid and the formation of the $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 / \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ compounds causes large volume expansion from the reaction surface which causes poor thermal shock resistance and eventual refractory failure. The hot face of an alumina-chromia refractory in service in an alkali environment will be prone to failure by alkali attack.

DISCUSSION OF CURRENT ACTIVITIES

During the present reporting period, a draft final report for this program was prepared and submitted for technical review and publication acceptance. Necessary clearances for publication of the report were recently received, and the report is now being prepared for printing and distribution.

577/578

PART V - ASSESSMENTS AND TECHNOLOGY TRANSFER

B&W-4 - POTENTIAL APPLICATIONS OF STRUCTURAL
CERAMIC COMPOSITES IN GAS TURBINES

W. P. Parks, R. R. Ramey, K. Smith,* and M. Van Roode*

Babcock & Wilcox
Lynchburg, Virginia 24506-1165

INTRODUCTION

The objective of this project is to determine the applicability of structural ceramics, especially ceramic composites, to land based turbines which are utilized in direct fired coal or coal gasifier combined cycled systems.

Background

Since their development, significant gains have been achieved in the technological advancement of land based turbines. Progress has been made in both materials and design with the vast majority of this effort directed towards the use of metallic materials. Contemporary gas turbines operate at maximum turbine inlet temperatures of 3050°F. It is probable that higher temperatures will be obtained in the future, however, any such gains will be marginal due to the inherent temperature limitations of the metal components themselves. To achieve a quantum leap in performance, the metallics in critical areas of the turbine must be replaced. Structural ceramic materials are the best replacement candidates as they offer high temperature stability and corrosion/erosion resistance superior to metals. Furthermore, the poor reliability of monolithic ceramics can be improved upon by using ceramic composites. Increasing the inlet temperature to 2450°F would permit an 8% increase in efficiency (Figure 1).

*Solar Turbines, Inc., San Diego, CA

Babcock & Wilcox is the prime contractor and Solar Turbines is a major subcontractor. Solar Turbines is a gas turbine designer and manufacturer.

Approach

This project is divided into three tasks. Under Task 1, Solar Turbines is reviewing and summarizing key elements of leading gas turbine designs for their applicability to both direct coal fired and coal gasification combined cycle systems. The summaries will include the chemical and physical conditions to which the materials will be exposed. For Task 2, Babcock & Wilcox is compiling a data base of existing monolithic and ceramic composite systems. From this body of knowledge, the applicability of promising materials to the components identified in Task 1 will be reviewed. For those turbine components for which no existing ceramic system is appropriate, the material research and development needs will be elucidated.

Using the results of Tasks 1 and 2, Task 3 will consist of the identification of gas turbine components for which the use of ceramic materials would result in the most significant improvement in operation and efficiency.

DISCUSSION OF CURRENT ACTIVITIES

Solar Turbines has identified twelve major system components for potential ceramic applications. These are distributed among four different areas (Table 1). The relationship of these four areas to each other and to other turbine components is shown in Figure 2. The operating conditions to which these components will be subjected in service are being summarized in an on-going literature search.

As part of Task 2, Babcock & Wilcox is compiling a data base on both monolithic and composite ceramics. Once the operating conditions of the gas turbine components have been identified, promising ceramic systems will be summarized using this body of knowledge. Monolithic ceramics under consideration include the oxides alumina and zirconia, and the non-oxides SiC and Si_3N_4 . Composite systems can be characterized as to whether the strengthening additive is particulate, whisker, or continuous fiber. Both oxide and non-oxide fibers and matrices are under review.

Table 1
Major System Components

Combustion Zone
Refractory Lining
Fuel Injector Nozzle Tips

Secondary Zone
Refractory Lining
Transfer Ducting

Hot Gas Clean-Up
Impact Separator
High Temperature Cyclones
Ceramic Candles
Woven Ceramic Bags
Cross-Flow Filters

Turbine Hot End
Turbine Nozzle Vanes
Turbine Rotor Blades
Scroll Section*

*Transfer ducting between cylindrical combustor and annular turbine.

Figure 1. Relationship of turbine efficiency vs inlet temperature

Figure 2. Schematic of land based gas turbine for coal gasification system.

BCL-4 - "MATERIALS AND COMPONENTS IN
FOSSIL ENERGY APPLICATIONS" NEWSLETTER

I. G. Wright

BATTELLE
Columbus Division
505 King Avenue
Columbus, Ohio 43201-2693

INTRODUCTION

The DOE Newsletter on Materials and Components in Fossil Energy Applications is intended as a vehicle to provide timely dissemination of information concerning developments in, or performance results of, materials and components in conventional or new processes for the utilization of coal, or for the conversion of coal to other energy forms. In recent years, emphasis has been placed on the direct utilization of coal as a chemical feedstock or as a fuel, rather than for providing a substitute for natural gas. Process efficiency and compliance with present and anticipated environmental regulations are two of the most important factors driving developments, and strongly influence not only new processes, but also existing systems.

The role of the newsletter has been to provide a guide to developing materials and components technology, and a forum for the presentation of the latest results and experiences.

DISCUSSION OF CURRENT ACTIVITIES

During this reporting period, three issues of the newsletter have been published. The articles in these editions were entitled:

Issue No. 73 (4/1/88)

- Wear in Mineral Processing Equipment
- Suppression of Fireside Corrosion of Boiler Waterwalls
- Erosion by Sand and Coal Slurries
- Workshop on Fireside Corrosion in Electric Utility Boilers
- METC Program on Wastage of Fluidized Bed Combustor Heat Transfer Tubes

Issue No. 74 (6/1/88)

- Tube Failure Incident at Black Dog FBC
- Experience at the Great Plains Coal Gasification Plant
- Review of Materials Requirements for Fluidized-Bed Combustion
- Ceramic Piston Bowl Inserts for Diesel Engines
- Transverse Cracking of Water Wall Tubes in Russian Boilers

Issue No. 75 (8/1/88)

- A Database for the Selection of Materials for High-Temperature Service
- Deposition in Coal-Fired Turbines
- Alloy Durability Data for FBC Air Heaters
- Erosion-Resistant Materials for Valves in Coal Gasifiers

ORNL-4(B) - COAL CONVERSION AND UTILIZATION PLANT SUPPORT SERVICES

J. R. Keiser and J. R. Mayotte

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

INTRODUCTION

Support services are currently being provided to two coal conversion facilities: the Advanced Coal Liquefaction Research and Development Facility at Wilsonville, Alabama; and the Morgantown Energy Technology Center's Hot Particulate Clean-Up Unit.

DISCUSSION OF CURRENT ACTIVITIES

During the last six months, activities involving the Wilsonville facility were failure analyses of pipe sections from the transfer line between the V1247 high-pressure separator and the E1212 reactor vapor cooler and supply, and monitoring of elastomer O-rings.

The analysis of the transfer line involved two pieces of 1.5-in. schedule 160 pipe and a 1.5-in. 6000-lb elbow that were sent to Oak Ridge National Laboratory (ORNL) for examination to determine the cause of cracking. The sections were reported to be made of type 316 stainless steel and had been part of the process line connecting the high-pressure separator, V1247, and the reactor vapor cooler, E1212, at the Wilsonville, Alabama, Coal Liquefaction Research and Development Facility. The temperature of V1247 is about 427°C (800°F), but between V1247 and E1212 this pipe is uninsulated so the temperature is reported to decrease considerably between the two pieces of equipment. Prior to failure of this pipe section, the Wilsonville facility switched to an Ohio bituminous coal that had a chlorine content of 0.16%.

For the examination, two sections were cut from the elbow in the area where cracking was evident. The samples were mounted and polished for metallographic examination, then an X-ray analysis system associated with a scanning electron microscope was used on one sample to check for the presence of chlorine. Photomicrographs were next taken of the samples in

the unetched and etched conditions. To confirm the composition of the pipe sections and elbow, the elemental content of the sections was determined with an X-ray fluorescence system.

The X-ray fluorescence analyses indicated that, for the elements checked, the sections all had the composition of type 316 (or 316L) stainless steel. Results are given in Table 1. Optical micrographs of both sections in unetched and etched conditions are shown in Figs. 1 and 2. These figures show that the cracking originated on the inside of the pipe and that it was of a transgranular nature with features typical of chloride stress corrosion cracking (SCC). An X-ray analysis was performed on one of the smaller cracks at the position shown in Fig. 3, and the analysis indicated that chlorine was present in the crack.

Apparently, an appreciable amount of chloride is present in the feed coal, and gaseous chloride species formed in the reactor vessel would be routed through this transfer line. According to the plant maintenance manager, the temperature drop that occurs in the transfer line between V1247 and E1212 is sufficient that condensation is expected in that line. For chloride SCC, an aqueous phase with dissolved chloride is required, and it appears that these conditions are present. The residual stresses associated with welding the pipes to the elbow likely provide the needed stress for SCC.

Given that the required environmental conditions are present, that chloride was detected in a crack, and that the metallographic examination showed transgranular cracking with the branching pattern characteristic of chloride SCC, it was concluded that chloride SCC was almost certainly the cause of this failure.

Table 1. Results of X-ray fluorescence analysis of elbow and pipe sections (wt %)

Element	Elbow	Long pipe section	Short pipe section	Nominal for type 316 SS
Ni	13.08	11.97	11.88	10-14
Cr	17.13	16.94	16.22	16-18
Mo	1.97	2.59	2.53	2.0-3.0
Ti	0.0	0.0	0.01	
Nb	0.01	0.0	0.08

Fig. 1. Photomicrographs of sample from type 316 stainless steel pipe showing (a) etched and (b) unetched areas. Note that cracks originate on the inner wall of the pipe, and cracking is transgranular.

(a)

200 μm

(b)

200 μm

Fig. 2. Photomicrographs of sample from type 316 stainless steel pipe showing (a) etched and (b) unetched areas. Note that transgranular cracking extends from the base metal into the weld metal.

Fig. 3. Scanning electron microscopy photograph of a small branch near a large crack. An X-ray analysis was performed on the region of the small branch crack at the point indicated.

Several approaches were suggested for preventing further cracking in this line. Chloride can be prevented from reaching this process stream, the temperature can be maintained high enough that an aqueous phase cannot form, or a material more resistant to chloride SCC can be used. If use of an alternate material is the control method to be used, we recommend that alloy 825 be tried based on our experience, and its availability and cost.

In a continuing effort to evaluate promising elastomeric materials, we have supplied and assessed the performance of O-rings in elevated temperature applications. O-rings made of the elastomer EPDM and obtained from two suppliers have been tested in several locations and have performed satisfactorily. The most recent information from Wilsonville engineers indicates that EPDM O-rings in the P-102C pump performed satisfactorily for 1440 h but had to be removed when they were damaged by the mechanical seal.

Four O-rings of Kalrez compound 3018 were purchased and sent to Wilsonville for evaluation in the P-1042 flash bottoms pump, an environment with especially high temperature and corrosive conditions. The set of O-rings installed in pump A lasted for 1440 h, while the set in pump B lasted 960 h. Process problems in the plant were reported to have contributed to the relatively short life of these O-rings.

Examination is nearly complete on four sections of Hastelloy C-276 pipe that were part of a heat exchanger in the Hot Particulate Cleanup Unit at the Morgantown Energy Technology Center. Techniques used include optical metallography, scanning electron microscopy, and electron microprobe. These techniques have enabled us to characterize the pipe in the areas of the failures, and a thermal analysis was done to estimate the temperatures reached in different sections of the pipe. Results of these examinations indicate that the penetration in the pipe was likely the result of internal sulfidation, but severe local oxidation also occurred in certain areas on the outside of the pipe. A failure analysis report is being written, and selected portions will be included in a future semiannual report.

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