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Fossil Energy Program

FOSSIL ENERGY PROGRAM SEMIANNUAL PROGRESS REPORT
FOR OCTOBER 1992 THROUGH MARCH 1993

R. R. Judkins
Program Manager

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April 1989 Through September 1989

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FOSSIL ENERGY PROGRAM SEMIANNUAL PROGRESS REPORT FOR OCTOBER 1992 THROUGH MARCH 1993 ¹

R. R. Judkins, Program Manager

ABSTRACT

This report covers progress made during the period October 1, 1992, through March 31, 1993, for research and development projects that contribute to the advancement of various fossil energy technologies. Projects on the Fossil Energy Program are supported by the DOE Office of Fossil Energy, the DOE Morgantown Energy Technology Center, the DOE Pittsburgh Energy Technology Center, the DOE Fossil Energy Clean Coal Technology Program, the DOE Fossil Energy Office of Petroleum Reserves, and the U.S. Agency for International Development.

1. INTRODUCTION

P. T. Carlson

The Oak Ridge National Laboratory (ORNL) Fossil Energy Program research and development activities, performed for the Department of Energy (DOE) Assistant Secretary for Fossil Energy, cover the areas of coal, clean coal technology, and support to the Strategic Petroleum Reserve. The principal focus of ORNL's fossil energy activities is coal, with emphasis on materials research and development; environmental, health, and safety activities; and bioprocessing of coal to produce liquid or gaseous fuels.

The Fossil Energy Program has projects in seven ORNL divisions (see Figure 1). Included as part of the Fossil Energy Program is the technical management of all activities on the DOE Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program. The AR&TD Materials Program includes research at six other DOE laboratories, at universities, and at industrial organizations. This Fossil Energy Program

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progress report, however, covers only those activities performed at Oak Ridge National Laboratory. Reports of work on the AR&TD Materials Program performed at other organizations may be found in the series of progress reports issued by the Fossil Energy AR&TD Materials Program.¹

1.1 MATERIALS RESEARCH AND DEVELOPMENT

Materials research and development activities at Oak Ridge National Laboratory consist of: ceramics development for high temperature applications, new metal alloys with unique mechanical properties, and corrosion research to understand the behavior of materials in coal combustion and conversion environments. The transfer of technology developed on this program is enhanced through interaction with industry and joint research programs with those interested in using the technology.

1.2 ENVIRONMENTAL ANALYSIS SUPPORT

Activities in environmental analysis support included assistance to the Morgantown and Pittsburgh Energy Technology Centers (METC and PETC) in preparing documents required by the National Environmental Policy Act (NEPA) for several projects selected for the Clean Coal Technology Program. A key activity was the preparation for PETC of a draft Environmental Impact Statement (EIS) for the Healy Clean Coal Project in Healy, Alaska. This document, which was released to the public in November 1992, is notable because it is the first site-specific EIS prepared for the Clean Coal Technology Program. In addition, a preliminary draft EIS was prepared for METC for the Des Moines Energy Center Repowering Project in Pleasant Hill, Iowa. This work is the second site-specific EIS and the first one prepared for METC. Another important activity was the preparation for METC of a preliminary draft Environmental Assessment (EA) for the proposed Gasification Product Improvement Facility (GPIF). This project is planned to be built at the existing coal-fired Fort Martin Power Station (FMPS) located north of Morgantown, West Virginia.

The Fossil Energy Program provides assistance to PETC in satisfying the NEPA requirements for the retirement and dismantling of the Advanced Coal Liquefaction Research and Development Facility in Wilsonville, Alabama.

1.3 COAL CONVERSION DEVELOPMENT

Fundamental bioprocessing research has concentrated on the use of biocatalysts in organic media and on advanced bioreactor systems. Coal conversion research has continued on the biological solubilization of coal using chemically-modified enzymes in organic solvents. Biophotolysis is being studied for the production of hydrogen. Activities are also continuing on the study of mild gasification of coal.

1.4 COAL COMBUSTION RESEARCH

It is known that fossil energy combustion devices, such as fluidized beds and pulsed combustors, can exhibit characteristic features of deterministic chaos. The ability to measure and describe chaotic components will contribute to greatly improved methods for characterizing, modeling, designing, and controlling commercial fossil energy processes such as combustion, coal gasification, hot-gas cleanup, and oil retorting. For these reasons, the Fossil Energy Program provides analytical support to METC in the evaluation of chaotic components in data from fluidized beds and other coal combustion processes.

In response to a request from the PETC, ORNL is providing technical assistance in the implementation of collaborative coal projects under the U.S. Agency for International Development (USAID)/Government of India Phase II, Alternative Energy Resources Development (AERD) Project.

1.5 FOSSIL FUEL SUPPLIES MODELING AND RESEARCH

ORNL is assisting the DOE Strategic Petroleum Reserve (SPR) Program through the assessment of alternative methods of financing oil acquisition and in the development of models for planning the capacity and management of the SPR.

1.6 COAL STRUCTURE AND CHEMISTRY

Research is also being conducted on the structure and chemistry of coal surfaces and interfaces to understand the complex processes and reactions occurring during the combustion of coal. Results have revealed that the hydrogen bonding structures of coal and the surface area of finely divided coal contribute significantly to the understanding of the properties of coal.

1.7 REFERENCE

1. *Proceedings of the Seventh Annual Conference on Fossil Energy Materials*, Oak Ridge, TN, May 11-13, 1993, ORNL/FMP-93/1, comp. N. C. Cole and R. R. Judkins, Oak Ridge National Laboratory, July 1993.

Fig. 1. Organization of the Oak Ridge National Laboratory Fossil Energy Program

2. MATERIALS RESEARCH AND DEVELOPMENT

N. C. Cole

This section describes research and development activities performed for the Fossil Energy Materials Program. Work on the Fossil Energy Materials Program includes the fabrication and characterization of fiber-reinforced ceramic composites, development of ceramic fiber-ceramic matrix hot-gas filters, development and testing of ceramic membranes for separation of gases, microwave sintering of materials for fuel cells, development of iron aluminides, studies of environmental effects of iron aluminides, development and evaluation of advanced austenitic alloys, evaluation of materials for hot-gas filter support systems, fundamental corrosion and oxidation studies, and materials testing and failure analysis support to coal conversion and utilization plants. Although not reported here, several technical transfer activities with industry are underway.

2.1 FABRICATION OF FIBER-REINFORCED COMPOSITES

D. P. Stinton, J. C. McLaughlin, and T. M. Besmann

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 react to deposit the ceramic matrix on and between the fibers.

Fiber composites are in the limelight as a result of the 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 consolidation technique has been used to prepare fiber composites with matrices of carbon or such ceramics as SiC, Si₃N₄, B₄C, BN, and TiB₂. Our goal is to demonstrate a rapid process for fabricating, via chemical vapor infiltration, 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 infiltrating process utilizing a thermal gradient combined with forced flow of the reactants is being pursued.

DISCUSSION OF CURRENT ACTIVITIES

The development of a process for the densification of tubular composites continued this period. Infiltration of these preforms using the current equipment configuration was unacceptably slow (about 150 hours) for two reasons. First, the temperature gradient was much too steep from the hot, outer diameter of the tube to the cool inner diameter resulting in very slow SiC deposition. Second, reactant gases appeared to be leaking past various seals and were not flowing through the fibrous preform. Modifications were made to the graphite gas distributor that increased the inner temperature from about 500°C to about 700°C. Additional modifications were made to the graphite fixturing to force the reactants through the preform. These modifications reduced the infiltration time by about 50% (i.e. tubes were densified in about 75 hours). Modeling efforts at the Georgia Tech Research Institute have indicated that the reactant gases are being depleted as they flow through the walls of the tubular preform. Optimization of the processing conditions will be investigated next period to further reduce the infiltration times.

Fiber-reinforced SiC matrix composites of thick-walled tubular geometry (2.5 cm ID by 0.6 cm wall thickness by about 15 cm long) were fabricated by forced chemical vapor infiltration for mechanical property testing at Virginia Polytechnic Institute. Mechanical properties have been measured on three composite tubes reinforced by very different fiber architectures (filament wound, cloth wrapped, and 3D braided). The axial stiffness of the cloth wrapped tube was measured at room temperature, 200°C, 400°C, and 600°C (Fig. 1). The axial stiffness of the braided and filament wound tubes (267 and 172 GPa, respectively) were also measured, but only at room temperature. The stiffness of the braided and cloth-wrapped tubes are much higher than the filament wound composite because more of the fibers are aligned in the axial direction. The axial stiffness of the cloth-wrapped tube compares very well with the tensile modulus (211 GPa) of cloth-layup composite plates reported by DuPont.

Fig. 1. Axial stiffness is controlled by the fiber architecture of the composite tubes.

The mechanical properties of the composite tubes were also measured in torsion. The shear modulus at room temperature was measured on the cloth-wrapped and 3D-braided tubes and found to be 94 and 128 GPa, respectively. During torsion testing, the filament wound tube fractured at a very low stress. This is understandable because fiber-reinforced composites are weakest in interlaminar shear. Cloth layup type composites have been observed to fail in shear between 15 and 35 MPa. Unfortunately, the filament wound composites fail by interlaminar shear if tested in axial tension or in torsion because of the fiber orientation. Therefore, filament wound composites would be useful for applications with high internal pressure (hoop stresses) but little or no axial or torsional stresses.

Nondestructive evaluation (radiography and computed tomography) was performed at ORNL prior to sending the tubes to Virginia Polytechnic Institute for mechanical property testing. Radiographs taken of the tubes clearly identified the orientation of the fibers within the tubes, but failed to reveal any significant porosity or flaws present in the composites.

Computed tomography of the composite tubes was much more revealing (Figs. 2-4). Computed tomography of filament wound tubes revealed large pores present within the walls of the tube. Evaluation of the 3D-braided tubes also revealed significant porosity particularly near the outer diameter of the tubes. Computed tomography of the cloth-wrapped composites revealed serious delamination within the walls of the tubes. These tubes were wrapped by hand and the cloth was held in place with graphite yarn. Alternate procedures need to be developed that can wrap the tubes to avoid delamination.

Bottom

Middle

Fig. 2. Large pores near the outer diameter of filament wound composites are observed by computed tomography.

Top

Middle

Fig. 3. Computed tomography reveals delamination within cloth-wrapped composites.

Bottom

Middle

Fig. 4. Large pores within 3D-braided composites are observed by computed tomography.

2.2 ALTERNATE INTERFACE COATINGS FOR NICALON®/SiC COMPOSITES

R.A. Lowden, K.L. More, N.L. Vaughn, and O.J. Schwarz

ABSTRACT

Boron nitride was examined as an improved interface coating for Nicalon®/SiC composites. The interlayers were deposited on fiber preforms from gas mixture containing boron trichloride, ammonia, and hydrogen employing a chemical vapor infiltration (CVI) technique. The preforms were subsequently densified with a silicon carbide matrix, and test bars prepared. Specimens were heated in air for 24, 100, and 1000 h at 1273 K, and for 100 h at 1473 and 1673 K. Room-temperature flexure strengths of as-fabricated and heat-treated composites were measured to assess the oxidation resistance of the fiber coating. Compositions and microstructures of the interlayers were characterized using electron microscopy. The composites with BN fiber coatings exhibited improved short-term (24 h) oxidation resistance as compared to those with carbon interlayers, but were embrittled by the heat treatment. Subsequently, strength was decreased and toughness was further diminished by extended exposure time and higher temperatures. Transmission electron microscopic analysis of the fiber-interlayer boundary revealed the presence of silica and carbon layers, products formed by the decomposition of the fiber. Thus the loss of strength and toughness appeared to be a result of chemical interaction between the fiber and oxygen in the BN interlayer, which was progressive with exposure time and temperature.

INTRODUCTION

Continuous fiber-reinforced silicon carbide matrix composites are being developed for use in high-temperature corrosive environments.^{1,2} These materials typically use a graphitic carbon fiber coating to limit the forces acting at the fiber-matrix interface and control mechanical properties.^{3,5} However, the poor oxidation resistance of the carbon interlayer limits the elevated temperature stability of these materials. For example, Nicalon®/SiC composites with a graphitic carbon interface layer exhibit properties favorable for use in fossil energy applications. These composites have thus been exposed to oxidizing and simulated fossil fuel environments to assess their stability.^{6,7} Composite specimens with and without an external SiC surface coating were oxidized in air and exposed to combustion environments at elevated temperatures. The mechanical properties of unprotected Nicalon®/SiC specimens were degraded after short periods of exposure, due to the oxidation and removal of the carbon interface coating. Longer exposures resulted in the oxidation of the fibers and matrix to form silica, which with time bonded the components together, and produced brittle behavior. The specimens protected by a SiC surface coating exhibited no decrease in strength after exposure to corrosive environments. The SiC layer sealed the surface of the composites, fibers ends, and thus

Nicalon®, Nippon Carbon Company, Tokyo, Japan.

prohibiting oxidation at the fiber-matrix interface. The surface coating was essential to protect the carbon interface from corrosion, however, efforts in the application of topical coatings and sealants to carbon-carbon composites have demonstrated that there are many difficulties associated with the use of protective surface layers.⁸ Processing flaws, and cracks in the coating caused by thermal expansion mismatch stresses or applied loads, can expose the substrate, leaving said susceptible to oxidation. Surface coatings would only be one component of a more complex protection system. A complete system may require combinations of surface layers, oxidation inhibitors, and environmentally stable fiber coatings.

To date, much of the work on interface coatings with improved oxidation resistance for use in silicon-based composite materials has paralleled the efforts to advance the elevated-temperature stability of carbonaceous materials.^{9,10} The efforts have focused on the development of glass formers, materials that upon oxidation produce a glass phase that can flow to seal the surface of the underlying substrate, hindering further attack. Silica functions well as a surface coating at temperatures >1500 K, however, at lower temperatures, the rate of oxidation is reduced, and in addition, the SiO_2 glass does not flow, limiting its effectiveness. Other glass formers have been studied, with boron being the most frequently utilized addition for temperatures around 1273 K.¹¹⁻¹³ Boron forms a glass with a melting point of ~ 725 K that can flow more readily at lower temperatures to seal the surface of the material to be protected.

Hexagonal boron nitride possesses a structure and mechanical properties similar to those of graphitic carbon, however, because of the presence of the boron, offers a distinct improvement in oxidation resistance.^{12,13} Due to the aforementioned similarities, it is expected BN could be used as a direct replacement for graphitic carbon as an interface coating in ceramic composites.¹⁴⁻²¹ Boron nitride interface coatings have proven to be useful in controlling chemical and mechanical interaction between fibers and matrices. Composites with good strength and toughness have been fabricated using BN-coated fibers and filaments.

This paper describes the investigation of BN as an alternative to graphitic carbon for the interface coating in Nicalon®/SiC composites. Boron nitride was deposited on the fibers from $\text{BCl}_3\text{NH}_3\text{-H}_2$ gas mixtures, and conditions were controlled to produce a fiber coating with a microstructure and properties similar to those of graphitic carbon. The composites were densified with silicon carbide employing the FCVI technique^{22,23} and the oxidation resistance of the composites assessed. The microstructure of the BN coating and the interfaces within the composites were characterized using electron microscopy to examine chemical interactions, and explain changes in observed mechanical behavior.

EXPERIMENTAL PROCEDURE

Composite Fabrication

Fibrous preforms were fabricated by stacking multiple layers of Nicalon® plain-weave fabric rotated in a $0 \pm 30^\circ$ sequence within the cavity of a graphite holder. The layers were hand compressed to produce a preform with a nominal fiber loading of 40 vol. % and were held in place by a perforated graphite lid pinned to the holder. The cloth sizing was removed through multiple washings with acetone. The sizes of the fibrous preforms were 45 mm in diameter and 12.5 mm thick, and 75 mm in diameter and 16 mm thick.

Preforms were coated with boron nitride interface layers from gas mixtures containing boron trichloride (BCl_3), ammonia (NH_3), and hydrogen (H_2), using a forced-flow, isothermal CVI approach with a preform temperature of 1373 K, and a reactor pressure of ≈ 5 kPa. The ratio of boron to nitrogen in the reactant gas mixture was held constant at unity. Reactant flows and concentrations were modified to produce: (i) deposition rates similar to those for the standard graphitic carbon layer, (ii) microstructures comparable to those of graphitic carbon, and (iii) a uniform layer thickness throughout the preform. Layer deposition times were then varied to control coating thickness. The final thicknesses of the interface layers were calculated from preform weight gains and also measured using electron microscopic analysis.

The preforms were densified with silicon carbide using the forced-flow, thermal-gradient chemical vapor infiltration (FCVI) process. The densification of porous structures using the FCVI process has been previously described in detail.^{1,14,15} The SiC matrix was produced by the decomposition of methyltrichlorosilane (CH_3SiCl_3 or MTS) in hydrogen at a hot-surface temperature of 1473 K and atmospheric pressure. The preforms were infiltrated with SiC to a maximum of 85 to 90 % of theoretical density in ≈ 20 h for the smaller samples, and ≈ 40 h for the larger.

Testing and Characterization

Test bars were cut from the samples parallel to the 0° orientation of the top layer of cloth using a diamond saw, and tensile and compression surfaces were ground parallel to the long axis of the specimen. The average dimensions of the specimens were 2.5 x 3 x 40 mm for those prepared from the smaller samples, and 3 x 4 x 50 mm from the larger composites. All specimens were measured and weighed to determine densities.

Specimens were oxidized in static air for 24, 100, and 1000 hours at 1273 K, and for 100 h

at 1473 and 1673 K. Flexure bars were placed on an alumina plate in the cavity of an atmospheric box furnace and heated to temperature at a rate of 300°/h. Once the furnace achieved equilibrium, the final temperature was measured using a hand-held optical pyrometer and then maintained using a thermocouple-controlled programmer. At the specified time, the furnace was shut off and allowed to cool unassisted.

Room-temperature flexure strengths for as-fabricated and heat-treated composites were measured in four-point bending. Support and loading spans of 25 and 6 mm, and 20 and 40 mm, were used for the smaller and larger specimens, respectively. A crosshead speed of 0.50 mm/min was used in all tests. The load was applied perpendicular to the layers of cloth. Load-displacement curves were recorded to examine the fracture process and determine the loads for ultimate strength calculations.

Fracture surfaces of the specimens were examined using a scanning electron microscope. Detailed characterization of interlayer composition and microstructure was accomplished using transmission electron microscopy (TEM). Specimens were prepared such that the area for analysis contained a quantity of fibers oriented perpendicular to the surface. The specimens were mechanically ground, polished, dimpled, and ion-milled to perforation using standard techniques. Microstructural characterization was conducted on a high resolution transmission electron microscope operated at 400 kV. The BN layers were also analyzed by parallel electron loss spectroscopy (PEELS), conducted at 100 kV using a transmission electron microscope with a field emission gun in the diffraction mode (image coupled).

RESULTS

Mechanical Properties

Typical load-displacement curves for the Nicalon®/SiC composites with boron nitride interface coatings of varying thickness are shown in Fig. 1. The composites exhibited good strength and composite behavior, and strength and toughness were influenced by coatings thickness (Table 1). Thicker coatings produced greater strain to failure, but also reduced strength beyond a given maximum.

Oxidation

The heat treatments produced a slight discoloration of all specimens suggesting some degree

of surface oxidation. The composites with the BN interface coatings of varying thickness exhibited good strength retention after the 24 h treatment at 1273 K (Table 1). The oxidized specimens, however, displayed lower toughness, as noted by a decrease in strain-to-failure, than for comparable untreated specimens.

Table 1. Properties of Nicalon®/SiC Composites with BN Interface Coatings (45 mm samples)

Deposition Time (h)	Interlayer Thickness (μm)	As-Fabricated Strength (MPa)	Post-Exposure Strength* (MPa)
1.0	0.20	417 $\pm$ 68	284 $\pm$ 63
2.0	0.47	406 $\pm$ 72	345 $\pm$ 36
2.0	0.42	419 $\pm$ 67	409 $\pm$ 76
4.0	0.63	389 $\pm$ 59	282 $\pm$ 62

* Heat treated in air for 24 h at 1273 K

Figure 1. Representative load-deflection curves for composites with BN interface coatings of varying thickness. [Curves are offset horizontally for clarity.]

With the exception of the samples heated at 1673 K for 100 h, the strengths and toughnesses of the composites with a $\approx 0.5 \mu\text{m}$ BN interface coating were degraded by the exposures (Table 2, Fig. 2). The extent of deterioration was dependent upon treatment time and temperature. In general, the samples possessed low strengths and showed little strain to failure. The aforementioned 1673 K samples also exhibited low strength, but possessed some degree of toughness as noted by extended strain to failure shown in the load-displacement curves in Figure 2.

Table 2. Flexure Strengths for Nicalon/SiC Composites with a $0.5 \mu\text{m}$ BN Interface Coating (75 mm sample)

Treatment	Flexure Strength (MPa)
as-fabricated	299 ± 87
100 h @ 1273 K	154 ± 30
1000 h @ 1273 K	172 ± 49
100 h @ 1473 K	124 ± 59
100 h @ 1673 K	139 ± 44

Figure 2. Representative load-deflection curves for heat-treated composites with a $0.5 \mu\text{m}$ BN interface coating.

Characterization

Transmission electron microscopic analysis of the BN fiber coatings found the layers to be composed of small, randomly-oriented hexagonal grains with $d_{002} = 0.33$ nm (Fig. 3). High-resolution TEM characterization of the BN layer-fiber interface in the as-fabricated state was conducted to examine chemical interactions that may have occurred during processing. No interaction was observed at the BN-fiber interface as noted by a clean transition from the featureless structure of the fiber to the polycrystalline nature of the BN coating. PEELS analysis of several BN interlayers in as-fabricated composites did reveal a significant amount of oxygen in the coatings (≈ 20 atomic %).

Microscopic characterization of the composites with BN fiber coatings after oxidation did reveal significant changes at the boundary between the Nicalon® fiber and the interface layer (Fig. 4). High resolution electron microscopy revealed a series of thin layers, beginning with an amorphous film close to the fiber surface, composed of SiO_2 , followed by a graphitic carbon layer. PEELS analysis of the two layers nearest the fiber surface found carbon and oxygen but no boron. In addition to the formation of the SiO_2/C sequence, there appeared to be a higher density of silicon carbide crystallites close to the surface of the Nicalon® fiber (indicated by arrows in Fig. 4). As exposure time and temperature were increased, the nature of the layers at the BN-fiber boundary was altered. Preliminary examination revealed changes in the composition and thickness of the layers, growth of the SiC grains, and the formation graphite "pockets", within but near the surface of the Nicalon® fiber.

Figure 3. TEM image of the BN coating in an as-fabricated Nicalon®/SiC composite. Inserts are a high-resolution image of the microstructure of the coating, and a single area diffraction pattern that confirms the random orientation of the grains.

Figure 4. TEM image of the BN/Nicalon® interface following oxidation of the composite for 24 h at 1273 K.

DISCUSSION

Hexagonal boron nitride has a crystal structure and properties similar to those of graphite, but exhibits better oxidation resistance.^{20,21} Hexagonal boron nitride is a very stable and involatile compound which is readily deposited employing chemical vapor deposition and infiltration techniques.^{20,22,23} It was hypothesized that due to its similarity to graphite, hexagonal BN could be used as a direct replacement for the carbon interlayer in ceramic matrix composites. This substitution has been suggested by others and BN has been examined as an interface coating in a multitude of fiber-reinforced ceramic composite systems, including Nicalon®/SiC composites fabricated employing chemical vapor infiltration techniques.^{9,22,23}

Boron nitride interface coatings have been deposited on Nicalon® fibers for use in CVI SiC matrices, using both BCl_3 ^{10,22} and boron trifluoride (BF_3)²³ as the boron-containing precursors. The trifluoride (BF_3) was chosen for isothermal, isobaric CVI (ICVI) studies because very slow deposition rates can be achieved using this reactant.²³ Slow deposition rates are required for ICVI processing

where the mechanisms of diffusion and reaction kinetics must be balanced to permit adequate penetration into the fibrous body and obtain uniform coating thicknesses. In the ICVI study, polycrystalline hexagonal BN coatings ($\approx 0.1 \mu\text{m}$ thick) were deposited on Nicalon® fiber preforms which were then infiltrated with a SiC matrix. The composites fabricated using said exhibited acceptable properties, comparable to composites with carbon interlayers of equal thickness. No information regarding the oxidation resistance of the composites was reported, however, a thin carbon-silica couple was found at the BN layer-fiber interface after processing. It was thought that the layers were produced by the decomposition of the Nicalon fiber.

In the presented and other efforts, BCl_3 was selected as the source of boron.^{10,22} In one of the earlier studies, amorphous BN interlayers were deposited on Nicalon® fiber tows, which were then densified with CVD SiC.²² The strengths of the "minicomposites" were measured and only the composites with BN coatings $> 1.0 \mu\text{m}$ in thickness possessed good strength and toughness. Heat treatments in air at 1323 and 1373 K for times of 50 and 70 h, respectively, produced no discernable changes in the mechanical properties of the materials.

The composites, described herewithin, were fabricated from Nicalon® fibers with BN interlayers. The composites exhibited mechanical properties, comparable to composites of similar composition but with a graphitic carbon interlayer.³ As for the composites with the carbon interface layers, the flexure behavior of the composites were influenced by the thickness of the BN fiber coating. Both strength and toughness were affected, and it was hypothesized that the low modulus BN layer acted, as did the carbon, to accommodate residual clamping stresses.¹⁹ These observations support the supposition that hexagonal BN can be used as a direct replacement for graphitic carbon as an interface layer in fiber-reinforced composites.

The fracture behavior of the composites was, however, altered by the 24 h exposure in air at 1273 K. Composite strength was slightly reduced for some of the samples, and failure was more brittle in all cases. As heat treatment time and temperature were increased, strength decreased, and in general, toughness was degraded. Notable changes in the fracture behavior of the composites, which varied with exposure conditions, were observed.

The loss of strength and toughness was unexpected, for the BN should have provided adequate oxidation resistance for the relatively short periods at moderate temperatures. High-resolution electron microscopy of the interfaces in the composites oxidized for only 24 h at 1273 K revealed significant changes at the fiber-BN boundary. A sequence of thin layers were found at the fiber-BN interlayer interface which consisted of an amorphous region, most likely SiO_2 , as determined by PEELS, followed by a carbon film immediately adjacent to the fiber. There was also evidence of a higher density of silicon carbide crystallites near the surface of the Nicalon® fiber. As exposure time

and temperature were increased, further changes in the microstructure and composition of the interface ensued.

The formation of the layers was observed in an aforementioned study of the same materials system,²² and as in the earlier study, fiber decomposition is suggested. The chemical interaction between the fibers and interlayer appeared to be induced by the presence of oxygen in the as-deposited BN. The decomposition of the fiber and changes at the fiber-interlayer boundary were most likely responsible for the degradation of composite strength and toughness. Time and higher temperature allowed the decomposition process to progress, complicating the nature of the fiber-matrix interface, and its influence on composite mechanical properties and fracture behavior.

CONCLUSIONS

Boron nitride interlayers improved the short-term oxidation resistance of the Nicalon®/SiC composites. Strengths and toughnesses of as-fabricated composites with BN fiber coatings were comparable to composites with graphitic carbon interlayers, and as with carbon interface coating, mechanical properties and fracture behavior were influenced by the thickness of the BN coating. Although strength loss after exposure in air at 1273 K for 24 h was minimal, toughness was diminished. In general, strength and toughness of the composites were further degraded by extended exposure and higher temperatures. The degradation of mechanical properties appears to be due to the decomposition of the fiber and chemical changes at the coating-fiber interface. It is hypothesized that oxygen contamination in the as-deposited BN layers caused the fiber to decompose, which lead to a decrease in reinforcement properties and a loss of composite strength and toughness.

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2.3 MICROWAVE SINTERING OF CERAMICS FOR FUEL CELLS

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ABSTRACT

Sintering of ZrO_2 -12 mol% CeO_2 was accelerated by microwave processing at 2.45 GHz as compared with conventional firing. However, the size of the "microwave effect" was significantly smaller than that which was previously observed for microwave sintering of ZrO_2 -8 mol% Y_2O_3 . The difference in the effect that the microwave field had on the two zirconia systems is interpreted in terms of their ionic conductivities.

INTRODUCTION

Microwave sintering of yttria-doped zirconia has been shown to reduce significantly the temperature required to achieve full density.^{1,2} Samuels and Brandon² further claim evidence for a reduction in the activation energy for sintering of zirconia by microwave firing. This reduction in processing temperature or activation energy is commonly called the "microwave effect".

Study of the sintering of ceria-doped zirconia allows examination of a system similar in chemistry to yttria-doped zirconia, but with significantly lower ionic conductivity.³ It is hypothesized that the lower ionic conductivity of the ZrO_2 -12 mol% CeO_2 should lead to a smaller microwave effect for this material.

EXPERIMENTAL PROCEDURE

This study was performed using commercial powders with composition ZrO_2 -12 mol% CeO_2 . All samples were formed by uniaxial pressing at 35 MPa (5 kpsi) in a 2.9 cm (1 1/8 in.) diam die, followed by isopressing at 210 MPa (30 kpsi). Samples for conventional firing weighed ~12g. Samples for microwave firing were significantly larger, typically 75g. Using a larger sample is related to the ability to heat the sample using

microwaves and to the ability to measure temperature accurately. Small samples do not couple efficiently to the microwave field and it is more difficult to measure their temperature. (Detailed discussions regarding the issues of sample size and temperature measurement in a microwave furnace can be found in references 4-9.) The microwave samples were made in two pieces, a top part (50g) and a bottom part (25g). A channel (~5mm wide x 5 mm deep) was cut into the top part using a ball-end mill to act as a thermocouple well. An alumina protection tube was placed around the thermocouple sheath to reduce the microwave field concentration at the thermocouple tip. A schematic view of the preferred arrangement for the sample and insulation is shown in Figure 1.

Figure 1. The preferred arrangement for firing ceria-doped zirconia at 2.45 GHz placed the sample within a porous alumina crucible, enclosed in yttria-doped zirconia bulk fiber insulation inside an alumina fiberboard crucible.

Both microwave and conventional furnaces were used in this investigation. The microwave furnace used in this study was built in-house. It consisted of a water-cooled aluminum microwave vessel, 70 cm (28 in.) diam by 120 cm (48 in.) long, with integral mode stirrer, forward and reflected power meters, microwave safety interlocks, ports for gas feeds, and thermocouple penetrations. Power was supplied by a 6 kW, continuously variable, 2.45 GHz microwave generator[‡]. A computer data acquisition and control program[†] was used to regulate the furnace and to log the temperature and power. Conventional furnace runs in air were made in a molybdenum disilicide element furnace.

DEVELOPMENT OF THE MICROWAVE FIRING TECHNIQUE

To be successful, the microwave firing technique used in this investigation had to fulfill at least three requirements: (1) provide indirect heating to the zirconia sample at low temperature; (2) provide a reasonable match between the dielectric properties of the insulation and the sample; and, (3) prevent contamination of the sample.

Developing a technique to uniformly sinter the ZrO_2 -12 mol% CeO_2 composition and meet the firing requirements outlined above was extremely challenging. Table 1 summarizes several of the different insulation and heating systems that were investigated. Fig. 2 shows four samples (Exs. 2, 3, 5, and 6) that resulted from microwave firing runs using the different insulation systems; Fig. 3 shows the heating curves (power and temperature vs. time) for these four samples.

One of the primary requirements for the insulation system was that it not contaminate the ZrO_2 -12 mol% CeO_2 composition of the samples. The first approach to this situation used a primary insulation that had the same composition as the sample. (The primary insulation is the material directly in contact with the sample, Fig. 1.) Specifically, the primary insulation consisted of granulated ZrO_2 -12 mol% CeO_2 powder, Table 1, Ex. 2. Fig. 2a shows that the result of this approach was less than satisfactory. The sample was conical in shape, having densified more on the top than on the bottom, which led to severe cracking caused by differential sintering. Apparently, a "hot spot" developed on the top side of the sample or in the insulation around the sample. The second approach was to blend the ZrO_2 -12 mol% CeO_2 powder with alumina bulk fiber insulation, Table 1, Ex. 3. Using the blend of alumina fiber and ZrO_2 -12 mol% CeO_2 powder resulted in somewhat more uniform heating but still did not produce a good pellet, Fig. 2b. The sample was convex in shape having bent toward the back side of the sample away from the thermocouple tip. In addition, a crack formed at the thermocouple well. At this point in the development of the insulation system it was thought that the insulation was not absorbing enough microwave energy. Hence, it might not be acting as a good "electric blanket"¹² to heat the sample to a temperature where it would couple on its own. In an attempt to increase the coupling of the fiber/powder blend, SiC grit was admixed with the insulation, Table 1, Ex. 5. This approach was disastrous, Fig. 2c. A large hot spot appeared on the bottom of the sample, which led to severe cracking. The insulation on the bottom of the sample actually fused, which indicated that the temperature was high enough to form a zirconia - alumina - silica glass in the insulation.

Table 1. Insulation systems investigated for firing $\text{ZrO}_2 - \text{CeO}_2$ at 2.45 GHz.

<u>Example</u>	<u>Pickets</u>	<u>Insulation*</u>	<u>Atmosphere</u>	<u>Results</u>
1	Yes	Granulated TZ12CE. Alumina fiber outer casket.†	Air	Uncontrolled excursions of power and temperature. Nonuniform heating, sample cracked.
2	Yes	Sample inside dense alumina crucible. Granulated TZ12CE.	Air	Severe cracking. Denser on top of sample, conical sample shape.
3	Yes	Mixture of TZ12CE w/ ALBF (3:1 w/w).	Air	Nonuniform heating, cracked. Sample is convex toward T/C well.
4	Yes	3:1 TZ12CE/ALBF. ZYC cylinder inside pickets.	Air	Banana-shaped sample.
5	No	3:1 TZ12CE/ALBF with 10 or 20 wt% addition of 400grit SiC.	Air	Severe heating on bottom of sample. Sample heavily cracked.
6	Yes	Sample inside dense alumina crucible. ZYBF primary insul'n.	Air	Sample sintered well.

* TZ12CE = zirconia - 12 mol% ceria powder, TOSOH USA, Atlanta.
 ALBF = alumina bulk fiber insulation, Zircar Inc., Florida, NY.
 ZYBF = yttria-doped zirconia bulk fiber insulation, Zircar Inc., Florida, NY.
 ZYC = yttria-doped zirconia fiberboard cylinder, Zircar Inc., Florida, NY.

† Used in all cases as the outer insulation and casket, AA30 alumina fiberboard cylinder, Zircar Inc., Florida, NY.

Figure 2. Examples of samples fired with different types of insulation systems described in Table 1. (a) Ex. 2; (b) Ex. 3; (c) Ex. 5; (d) Ex. 6.

There were two keys to developing a workable insulation system for firing the ZrO_2 - 12 mol% CeO_2 samples. The first was to use yttria-doped zirconia bulk fiber (ZYBF) as the primary insulation around the sample. The second was to put the sample inside an alumina refractory crucible. ZYBF insulation couples strongly with the microwave field at temperatures above $\sim 400^\circ\text{C}$. Therefore, it acted as a good “electric blanket” to provide secondary heating to the sample at temperatures between ~ 400 and 700°C , which was in addition to that provided by the picket fence below $\sim 400^\circ\text{C}$. The auxiliary heating provided by the ZYBF insulation allowed the samples to be heated uniformly. Hot spots in the insulation package that might lead to nonuniform sintering of the sample were thereby avoided. The alumina crucible provided a physical barrier between the sample and the zirconia bulk fiber insulation, which prevented contamination of the samples by yttria, Ex. 6 in Table 1, and Fig. 2d. It also provided a more even thermal barrier at the sample surface, which helped to keep the temperature more uniform. A schematic of the preferred experimental setup is shown in Figure 1.

RESULTS AND DISCUSSION

Sintering curves for conventional and 2.45 GHz microwave firing in air are shown in Figure 3. The samples that were microwave fired reached higher densities at a given temperature than those that were conventionally fired. The samples are completely in the tetragonal zirconia phase, as determined by X-ray diffraction. Normal microstructures were obtained for both the conventional and the microwave fired samples.

For the ZrO_2 - 12 mol% CeO_2 samples, there was a shift in the sintering curves of about 50°C for the microwave fired samples as compared with the conventionally fired samples over the entire range of densification. The average grain size for the conventionally fired sample ($d = 0.93\ \mu\text{m}$ @ 97.4% td) was larger than that for the microwave-fired sample ($d = 0.77\ \mu\text{m}$ @ 97.5% td) when compared at the same densities, Figure 4. Grain sizes were determined using the lineal intercept method.¹⁰ Both of these observations are consistent with the presence of a microwave effect for the sintering of ceria-doped zirconia. If no microwave effect existed, there should be no differences in the sintering curves or in the microstructures.

The shift in the sintering curves for microwave and conventional sintering of ZrO_2 - 12 mol% CeO_2 was much smaller than that observed for the sintering of ZrO_2 - 8 mol% Y_2O_3

Figure 3. Sintering curves for ZrO_2 - 12 mol% CeO_2 in air, conventional and 2.45 GHz microwave furnaces. Sintering curves for ZrO_2 - 8 mol% Y_2O_3 included for comparison. Curves for the yttria-doped samples are offset by 10% in density.

examined in a previous study.¹ As is shown in Fig. 3, the difference in sintering temperature between the microwave and conventionally fired yttria-doped zirconia samples was $\sim 100^\circ\text{C}$ over most of the range of density and increased to as much as 175°C at the highest densities. In addition, the differences in grain size between conventional and microwave firing was different for the ceria- and yttria-doped systems. The ratio of conventional to microwave grain size in the ceria-doped system was 1.2 to 1; for the yttria-doped system it was 1.6 to 1. Thus the ceria-doped zirconia exhibited a smaller microwave effect than the yttria-doped system both in terms of densification enhancement and grain size reduction.

The reason for the difference in the magnitude of the microwave effect for these two zirconias is thought to be the differences in their ionic conductivity. The ionic conductivity of the ZrO_2 - 8 mol % Y_2O_3 samples is >100 times that of the ZrO_2 - 12 mol% CeO_2 samples over a wide range of temperature.³ The higher conductivity is caused by the substitution of the Y^{+3} ion onto the Zr^{+4} site in the zirconia lattice, which creates oxygen vacancies to balance the charge in the lattice. This increase in the concentration of oxygen vacancies in the lattice increases the ionic conductivity. In the case of Ce^{+4} substituting for

(a)

(b)

Figure 4. The average grain size, d , for ZrO_2 -12 mol% CeO_2 sintered in air was larger for conventional sintering than for microwave sintering. Polished section; thermal etch 1h at 1150°C to reveal grain boundaries; SEM micrograph; (a) conventional firing, $\rho = 97.4\%$ td, $d=0.93\ \mu\text{m}$, $T_{\text{sinter}} = 1450^\circ\text{C}$; (b) microwave firing at 2.45 GHz using procedure of Ex. 6, $\rho = 97.5\%$ td, $d=0.77\ \mu\text{m}$, $T_{\text{sinter}} = 1400^\circ\text{C}$. Grain size was determined using the lineal intercept method.¹⁰

Zr^{+4} , no additional vacancies are created and the ionic conductivity is not significantly increased. The predominant mechanism by which microwaves interact with an oxide ceramic is through defects in the structure of that material.¹¹ Therefore, it is reasonable to expect that a material with a higher concentration of defects should absorb more microwave energy and should heat more readily than one with a lower concentration of defects. This was indeed observed: the ceria-doped zirconia was more difficult to heat than the yttria-doped zirconia.

CONCLUSIONS

A "microwave effect" was observed for the sintering of ZrO_2 -12 mol% CeO_2 at 2.45 GHz. This manifested itself as a shift in the sintering curve to lower temperature for microwave heating as compared with conventional heating. The grain size of the microwave fired samples was smaller than that of the conventionally fired samples. The magnitude of the microwave effect observed for ceria-doped zirconia in this study was substantially smaller than that observed previously for yttria-doped zirconia. The shift in sintering curves in the present study was only $\sim 50^\circ\text{C}$ as compared with $\sim 100^\circ\text{C}$ in the previous study. Also, there was a smaller difference in the ratio of grain sizes of conventional to microwave samples in the present study (1.2:1) as compared with the previous study (1.6:1).

NOTES

* TOSOH U.S.A., Inc., Atlanta.

‡ Cober Electronics, Stamford, Conn.

† LabVIEW®, National Electronics, Inc., Dallas.

Keith Co., Inc., Pico Rivera, CA.

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2.4 ENVIRONMENTAL EFFECTS ON IRON ALUMINIDES

J. H. DeVan and P. F. Tortorelli

INTRODUCTION

The high temperature properties of iron-aluminum alloys are being studied to characterize their behavior in coal-derived environments. The work includes investigation of effects of sulfur on oxidation kinetics and oxide microstructures, the effects of reactive metal additions on sulfidation and oxidation resistance, and the mechanical behavior of reaction product scales in mixed-gas environments. Of additional concern are corrosion processes which may lead to attack by sulfur- and chlorine-containing acids when equipment is shut down for maintenance purposes.

Laboratory tests of iron aluminide alloys in H_2S - H_2 - H_2O -Ar at 700-800°C have shown very low corrosion rates for alloys based on Fe_3Al and FeAl .^{1,2} In more recent tests of binary Fe-Al alloys with lower aluminum contents, the corrosion rate in H_2S - H_2 - H_2O -Ar showed little change from that of the Fe_3Al alloy (28% Al*) down to a level of 18% aluminum.^{3,4} The corrosion rate increased significantly when the aluminum was lowered to 16%, although it was still below that for an alloy containing Fe-18%Cr-10%Al. A concentration of 20% Al was found to be required for sustained oxidation resistance of binary iron-aluminum alloys in dry air at 900°C and above.

Further corrosion studies have been conducted to evaluate the potential of alloys containing $\geq 16\%$ Al for service in high temperature air and mixed gases and to characterize the resistance of reference Fe_3Al -based alloys to both high temperature oxidizing and sulfidizing environments. Laboratory tests are being conducted to evaluate corrosion properties under isothermal and thermal cycling conditions in controlled environments, and selected alloys are also being exposed in an oxygen-blown, pressurized gasifier operated by the Coal Research Establishment (British Coal) in the United Kingdom.

EXPERIMENTAL PROCEDURES

Reference Fe_3Al alloys listed in Table 1 were obtained from outside vendors and were supplied in the form of 50-100 kg billets that were subsequently rolled to sheet at

*Concentrations denote atomic percent.

TABLE I. Compositions of Reference Alloys (Atomic %)

Alloy Designation	Al	Cr	Nb	Mo	Zr	Other
FAS	28	2				0.05B, bal Fe
FA129	28	5	0.5			0.1C, bal Fe
FAP	16	5		1.0	0.1	0.1C, bal Fe

Oak Ridge National Laboratory (ORNL). Other iron-aluminum compositions were prepared at ORNL by arc-melting high-purity component metals under argon and drop casting into a water-cooled copper mold. They were then hot- and warm-rolled to plate with a final thickness of 0.75 mm. All materials were given a final anneal for 1 h at 700°C. Rectangular specimens, approximately 16 by 7 mm, were prepared and mechanically abraded on the two major surfaces, ending with 600-grit abrasive. Corrosion rates were determined by continuous weight change measurements in the case of isothermal tests and by periodic weight change measurements in thermal cycling tests. The test environment was composed of either a 5.4% H_2S -79.4% H_2 -1.64% H_2O -13.6%Ar (by volume) gas mixture or laboratory (dry) air and was replenished at a rate of 2 cc/s. Thermal cycling experiments were conducted in horizontal tube furnaces. Specimens were withdrawn at intervals of 24-72 h, cooled to room temperature, weighed, and returned to the furnace.

RESULTS AND DISCUSSION

The effect of chromium is an important consideration in selecting Fe_3Al alloy compositions for field tests in operating coal combustors and gasifiers. Compositions containing 5% Cr are more resistant to attack by combustion environments containing alkali sulfates⁵ and also to attack by sulfur acids⁶ occurring during downtime periods. However, those with chromium concentrations $\leq 2\%$ are more resistant to oxygen-deficient product gases generic to coal gasifiers.² Accordingly, a Fe_3Al alloy containing 5% Cr (FA129) has been targeted for combustion service, while another one containing 2% Cr (FAS) is recommended for gasifier service. Laboratory tests of these reference alloys in air and mixed gas were conducted to directly compare their corrosion resistance under purely oxidizing and oxidizing/sulfidizing conditions.

Fig. 1. Comparative weight gains of FAS (28Al-2Cr) and FA129(28Al-5Cr) in H_2S - H_2 - H_2O -Ar at 800°C .

Weight change results for H_2S - H_2 - H_2O -Ar exposures at 800°C are shown in Fig. 1. After 168 h, the weight gain of the FA129 alloy containing 5% Cr was ten times greater than that of the FAS alloy containing 2% Cr. Weight increases for both alloys subscribed to a $t^{1/2}$ time dependence, and the respective parabolic rate constants are compared in Table 2. The rate constant for the 2% Cr alloy reflects the growth of an essentially pure, uniform Al_2O_3 scale, whereas the corrosion product scale on the 5% Cr alloy is composed of iron and chromium sulfide platelets on the gas side and an aluminum-rich inner layer containing Al_2O_3 and Al_2S_3 .¹ Although the addition of chromium to Fe_3Al obviously decreases its corrosion resistance to H_2S under the highly reducing conditions typical of gasifiers, the corrosion rate is still well below that of Fe-Cr-Al alloys containing lower aluminum and higher chromium concentrations. For example, in tests of developmental Fe-18%Cr-6%Al alloys (wt%) supplied by Harwell Laboratory,³ parabolic rate constants under our reference mixed gas conditions were a factor of 3000 higher than those for the Fe_3Al - 5% Cr alloys. It was also previously shown^{2,7} that spalling of the initial corrosion product scale formed on 5% Cr alloys, which occurs on cooling to room temperature, acted to reduce the corrosion rate during subsequent exposure to the mixed gas. The longer the initial exposure, the lower the corrosion rate during subsequent exposure, and after a 168-h initial exposure, the corrosion rate approached that for the 2% Cr alloys. Thus, while the results of these laboratory tests confirm the superior corrosion properties of the 2% Cr alloy under gasifier conditions, the 5% Cr alloy should not be eliminated from consideration for this application. Accordingly, both alloys are being evaluated in field tests in the British Coal gasifier cited above.

TABLE 2. Parabolic Rate Constants for Reference Alloys at 800°C

Alloy Designation	Kp (Mg ² cm ⁻⁴ s ⁻¹) X 10 ⁸	
	Mixed Gas	Dry Air
FAS	4.69	2.14
FA129	106.94	(2.0 - 3.0) ^a

^a Rate constants decrease with exposure time

Fig. 2. Comparative weight gains of FAP (16%Al-5%Cr) and FA129 (28%Al-5%Cr) in H₂S-H₂-H₂O-Ar.

Fig. 3. Comparative weight gains of FA129 (28Al-5Cr) and FAP (16Al-5Cr) in dehumidified air at 900°C.

Studies of iron-aluminum alloys have included the FAP composition (Table 1) which contains 16% Al and 5% Cr. This alloy is relatively ductile at room temperature and can be easily formed into wire and thin sheet products. However, as reported previously,³ the aluminum content is below the level required ($\geq 18\%$) for optimum corrosion resistance in mixed gas. Figure 2 compares the weight change of the FAP alloy in $\text{H}_2\text{S-H}_2\text{-H}_2\text{O-Ar}$ with that of FA129. After 40h at 800°C , the weight gain of the 16% Al alloy is about a factor of seven greater than that of FA129. (The corrosion rate of FAP appears to have a parilinear time dependence, and therefore the rate constant can not be directly compared with those for the higher Al alloys.) Nevertheless, the corrosion rate of the FAP alloy was still significantly below that of the Fe-18Cr-10Al family of alloys under the reference mixed gas exposure conditions.

The FA129, FAS, and FAP alloys exhibited essentially equivalent corrosion rates in isothermal exposures to dehumidified air at $800\text{-}1000^\circ\text{C}$. Weight gains for the FA129 and FAP compositions at 900°C are compared in Fig. 3. The scales formed in air were chemically similar for all alloys, i.e., they contained only aluminum with no iron or chromium. As discussed previously,^{3,8} chromium additions to Fe_3Al alloys tend to slightly accelerate their oxidation in air. Unlike the case for mixed gas, however, the higher rate in air occurs primarily during the early (transient) stage of oxidation, and during the later stages (≥ 100 h), the respective rate constants converge. This later oxidation stage appears to be associated with the growth of $\alpha\text{-Al}_2\text{O}_3$, and the earlier stage with a metastable form of alumina. Thus, the presence of chromium in the alloy appears to increase the growth rate of the transition Al_2O_3 phase, and, as a consequence, accelerates the initial oxidation rate of the 5% Cr alloys compared to lower chromium alloys such as FAS. This is very different from the effect of chromium in mixed gas where it promotes the growth of sulfide-containing corrosion products. Acceleration of the initial growth rate of Al_2O_3 by chromium is also believed to contribute to the excellent oxidation properties of the FAP alloy containing 16% Al. As discussed elsewhere,⁴ the role of chromium in alloys containing 16% Al is to inhibit the growth of iron oxide nodules in the scale, which significantly compromises the oxidation resistance. The nodules, which appear to develop at mechanical flaws in an otherwise protective Al_2O_3 scale, are completely suppressed by the addition of 5% Cr. Since no chromium-containing species have been detected at any stage of layer development, chromium appears to accelerate the growth of "new" Al_2O_3 , thereby offsetting nodule growth when flaws develop.

The rate constant governing scale growth on the FAS alloy (2% Cr) was a factor of two greater in mixed gas than in air (Table 2). The higher corrosion rate in mixed gas compared to air must relate to an effect of sulfur on the growth kinetics of Al_2O_3 , since this was the only product found in the scale in either environment. The exact mechanism of the sulfur effect remains to be identified, but possibilities include an influence of sulfur on the defect structure of the scale or the stabilization of a transient form of alumina.

Another component of the studies with iron aluminides involves cyclic oxidation behavior. Measured weight changes under cyclic conditions were previously reported for air exposures at 900, 1000, and 1150°C.⁹ The weight changes of the 16% Al alloys containing chromium were not much different from the aluminide containing 28% Al. Further analyses showed that differences in the cyclic oxidation response of various iron aluminide compositions correlated with differences with the appearance of the as-oxidized surfaces. Within the first few cycles, the FAP scale developed a fairly uniform color (medium to dark gray) and texture, much like the adherent scales that formed on certain Fe_3Al alloys. On the other hand, the binary alloys with 16 and 20% Al appeared to have mixed surface products (reddish-brown as well as gray regions) and experienced some loss of reaction product, principally during the initial stages of exposure (despite showing weight increases after nearly every cycle). However, none of the cyclically oxidized alloys showed visual evidence of substantial spallation to bare metal.

After the final exposure cycle, the specimens were examined by scanning electron microscopy (SEM) and associated energy dispersive x-ray analysis (EDX). The scales formed on the 16% Al binary aluminide at 900 and 1000°C (Fig. 4) were significantly rougher and exhibited more cracks than those on Fe - 20% Al (Fig. 5). The scale on the 20% Al alloy, in turn, appeared to be thicker than that found on the surface of cyclically oxidized FAP (Fig. 6). A typically oxidized surface of thermally cycled Fe_3Al is shown in Fig. 7. Some evidence of in-scale spallation was observed. Despite the morphological differences in scales formed on the various aluminide compositions, the predominant cation surface element in all cases was aluminum, which is consistent with the formation of an alumina surface product. Relatively few iron-enriched nodules were found despite the visual observations of a reddish product on surfaces of the binary alloys with 16 and 20 % Al. Most were concentrated on the 20% Al specimen exposed at 1000°C. (One is shown in the upper central part of Fig. 5). These were much different from the small nodules found on the FAP surface (Fig. 6). EDX analysis found that the latter nodules had compositions much like that of the underlying aluminum-rich scale.

Fig. 4 - Scanning electron micrograph of Fe - 16% Al cyclically oxidized in air at 1000°C for 706 h.

Fig. 5 - Scanning electron micrograph of Fe - 20% Al cyclically oxidized in air at 1000°C for 706 h.

Fig. 6 - Scanning electron micrographs of FAP cyclically oxidized in air at 1000°C for 706 h.

Fig. 7 - Scanning electron micrograph of Fe - 28% Al - 5% Cr - 0.1% Zr cyclically oxidized in air at 1000°C for 695 h.

The finding that the cyclic oxidation resistance of FAP was significantly better than that of the binary composition (16% Al) is consistent with results from isothermal experiments.^{4,10} Under isothermal conditions, the addition of approximately 5% Cr to the Fe-16% Al binary alloy substantially decreased the oxidation rate, and further alloying to obtain the base composition of FAP reduced it even more so as to be nearly comparable to that for 28 at.% Al alloys.^{4,10} In addition, it has been shown^{3,11} that the presence of zirconium significantly improves the spallation resistance of the Fe-28% Al-Cr alloys under thermal cycling conditions like those of the present study. In the case of the 16% Al alloys, it is clear that those containing Cr and Zr show improved cyclic oxidation resistance, although the individual effect of Zr has not been resolved.

After cyclic oxidation the SEM/EDX examination of the chromium-containing specimens showed scale morphologies that were generally consistent with those previously found after isothermal exposures; that is, there was no evidence of iron oxide nodules even at aluminum concentrations as low as 16% (ref. 4). Likewise, the overall compositions of the surface scales showed mainly aluminum and negligible iron. When coupled with the observation that chromium accelerates the initial oxidation rate of Fe-28% Al (ref. 8), a mechanism is again suggested in which this element promotes the rapid healing of the defects in the Al_2O_3 scale that normally serve as the sites for growth of iron oxide (see above).

The scale morphologies of the binary alloys containing 16 and 20% Al were inconsistent with results of earlier isothermal experiments and with each other. Iron oxide nodules were detected in the case of the latter alloy but not the former, the opposite of what was found for isothermal exposures.⁴ Furthermore, the iron concentration of the scales, as detected by EDX, was greater for the 20% alloy than for the 16% alloy. One possible explanation for this anomaly may be a loss of the iron-rich products during thermal cycling (which increases with the volume of nodules). As noted earlier, the 16 % Al binary alloy showed some reddish-brown color normally indicative of iron oxides, possibly a remnant of a larger concentration that had been lost on thermal cycling.

The results of the present thermal cycling work demonstrate that the cyclic oxidation resistance of 16% Al-Cr-Zr alloys is of the same order as that of Zr-containing Fe_3Al -based (28% Al) alloys despite the significant difference in aluminum concentrations. However, the frequency of thermal cycles used in these experiments was low. Under harsher conditions, typical of many studies and some applications, spallation is more likely to occur. In the presence of repeated, substantial scale spallation, a difference between Fe-16% Al and Fe-28% Al alloys could result because of depletion of aluminum in the alloy near the oxide-metal

interface, which could ultimately compromise the ability of the alloy with 16% Al to maintain a protective alumina scale.

SUMMARY

The corrosion rates of reference of Fe₃Al-based compositions containing 2 and 5% Cr were compared in a mixed gas composed of H₂S-H₂-H₂O-Ar. The parabolic rate constant at 800°C for Fe₃Al-5% Cr was a factor of 200 higher than that for Fe₃Al-2% Cr. Similar exposure of an alloy containing 16% Al and 5% Cr resulted in significantly higher weight gains than the Fe₃Al-5% Cr composition. However, all the alloys were significantly more resistant to the mixed gas than iron-based alloys with higher chromium and lower aluminum contents.

Aluminides with 16 % Al and additions of chromium (5%) and zirconium (0.1%) showed improved cyclic oxidation resistance in air at 900 and 1000°C relative to binary alloys of 16 and 20% Al. The extent of oxidation of these 16% Al alloys was comparable to Zr-containing Fe₃Al aluminides (28% Al) that develop adherent scales. More aggressive thermal cycling conditions (higher cycle frequencies) may compromise the ability of these iron aluminides to provide protection at high temperatures, particularly those alloys containing lower concentrations (16%) of aluminum.

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2.5 Cr₂Nb DEVELOPMENT

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ABSTRACT

Microstructure and mechanical properties of Cr-Nb alloys containing 5.6 to 17% Nb were studied for high-temperature structural applications. The alloys basically contain the two phases of Cr₂Nb and chromium-rich solid solution. Alloying additions including Re, Al, Ni, Fe, and Co were added to the alloys for control of microstructure and properties. The alloys show an excellent strength at temperatures to 1250°C. Among the alloying elements, rhenium is found to be most effective in improving the mechanical properties at room and elevated temperatures. Alloying with $\leq 8\%$ Al, Ni, and Co, on the other hand, lowers the strength and ductility at elevated temperatures. Further development is required to improve the fracture resistance of the alloys at ambient temperatures.

INTRODUCTION

The objective of this task is to develop new-generation high-strength, corrosion resistant intermetallic alloys based on Cr₂Nb for use as critical hot components in advanced fossil energy conversion systems. The intermetallic phase, Cr₂Nb, with a C-15 complex cubic structure,¹ has been selected for this development because of its high-melting point (1770°C),^{2,3} relatively low density (7.7 g/cm³),⁴ and potential resistance to oxidation and corrosion.² This intermetallic phase, as well as many other Laves phases has a wide range of compositional homogeneity,³ suggesting the possibility of improving its mechanical and metallurgical properties by alloy additions.

The major concern with Cr₂Nb and other A₂B Laves phases is their poor ductility and fracture toughness at ambient temperatures.^{2,5,6} The single-phase Cr₂Nb is very hard (~800 DPH) and brittle at room temperature. As a result, the development effort has been concentrated on two-phase structures containing the intermetallic phase Cr₂Nb and the chromium-rich solid-solution phase. Previous studies indicated that the two-phase alloys exhibited plastic deformation under compression at room temperature, with strength substantially better than nickel-based superalloys at and above 1000°C.^{5,7} Bhandanker^{8,9} had demonstrated that a dispersion of TaFe₂ Laves-phase particles dispersed within grains of a ferritic steel produced good high-temperature strength without low-temperature

embrittlement. Recently, considerable effort has been devoted to the development of Laves-containing superalloys for high-temperature structural use.^{5-7,10-15}

The results obtained so far indicate that the $\text{Cr}_2\text{Nb}/\text{Cr}(\text{Nb})$ alloys have excellent strength for structural use at ultrahigh temperature (e.g., 1000-1300°C).^{5,7} Potential applications include hot components in advanced fossil energy conversion systems, advanced heat engines, and high-temperature cutting and grinding tools. The alloys, on the other hand, suffer poor tensile ductility and fracture resistance at ambient temperatures. They showed some oxidation resistance at 950°C, but exposures can result in spallation of oxide scales at this temperature.¹⁶ This paper summarizes our recent alloy development effort on improving the mechanical and metallurgical properties of $\text{Cr}_2\text{Nb}/\text{Cr}(\text{Nb})$ alloys through control of (1) the amount of the Cr_2Nb phase, (2) the impurity level in alloys, and (3) dispersion of Cr_2Nb in the $\text{Cr}(\text{Nb})$ matrix by alloy additions. A detailed study of the corrosion behavior of these alloys is reported separately by Tortorelli et al.^{16,17}

ALLOY PREPARATION AND FABRICATION

$\text{Cr}_2\text{Nb}/\text{Cr}(\text{Nb})$ alloys weighing 300 g were prepared by arc melting and drop casting in copper molds. In order to reduce the interstitial impurity (e.g., oxygen) in the alloys, high-purity niobium and chromium metal chips were used as charge materials, and the alloys were melted in a high vacuum (10^{-5}Pa) furnace. Cast molds were preheated to 100-300°C in order to control alloy solidification and to reduce microporosity formation during drop casting.

Table 1 lists the composition (at. %) of CN (Cr-Nb) alloys used in the current study. The alloys contain 5.6-17% Nb with and without alloying additions. A systematic study was made on the 12% Nb alloys containing Al, Ni, and Co. Chemical analyses indicate that the high-purity alloys contain less than 200wt ppm interstitials (oxygen and carbon). In comparison, similar alloys prepared previously contained interstitials at levels of 700-1000 wt ppm. High purity, together with preheating, appear to eliminate microcracks in most alloys (except CN-47 and 48); however, some shrinkage microcavities with diameters as big as 20 μm were observed in the cast ingots.

In order to explore the hot fabricability of Cr_2Nb -base alloys, the alloy ingot CN-43 was clad in molybdenum sheets and hot forged at 1100-1200°C in air. The alloy cracked badly after a reduction in thickness of 25%. This result indicates that the alloy containing 12% Nb possesses limited hot fabricability.

Table 1. Alloy Composition of CN alloys

Alloy number	Composition (at. %)		
CN-7	Cr-6 Nb		
CN-4	Cr-12 Nb		
CN-45	Cr-17 Nb		
CN-43	Cr-12Nb-4Re	-2Al	-0.03Y
CN-44	Cr-12Nb-4Re	-2Al	-0.2Hf
CN-46	Cr-12Nb	-8Al	
CN-47	Cr-12Nb	-12Al	
CN-48	Cr-12Nb	-16Al	
CN-49	Cr-12Nb	-8Ni	
CN-50	Cr-12Nb	-12Ni	
CN-51	Cr-12Nb	16Ni	
CN-56	Cr-12Nb-4Re	-2Al-10 Co	
CN-57	Cr-12Nb-4Re	-2Al-20 Co	
CN-58	Cr-12Nb-4Re	-2Al-30 Co	
CN-52	Cr-5.6Nb-4Re	1.5Al	-0.1Hf
CN-53	Cr-5.6Nb	1.5Al-2Ni-2Fe	-0.1Hf

EFFECT OF NIOBIUM CONCENTRATION ON STRUCTURE AND PROPERTIES

The chromium-niobium phase diagrams published recently indicate that the Cr_2Nb -Cr(Nb) eutectic composition is located at 17 at. % Nb.⁵ Based on the phase relationship, three alloys containing near eutectic composition (17% Nb) and hypoeutectic compositions (12 and 6% Nb) were prepared, and compression specimens with dimensions 6-mm-diam. x 9-mm height were machined by electrodischarge machining (EDM) and grinding. The alloy specimens annealed at 5/d 900°C or 3/d 1100°C and then tested at room temperature in air under compression. Table 2 summarizes the compressive properties. With increase in niobium concentration (or vol. fraction of Cr_2Nb), the yield strength increases and the ductility decreases sharply. As shown in Table 2, the 17% alloy fractured prior to macroscopic yielding at room temperature. Thus, the niobium content in the CN alloys should be much less than 17%. The maximum solubility of niobium in the chromium-rich phase is around 6%, hence the control of dispersion of Cr_2Nb particles is much easier in the alloys with $\leq 6\%$ Al.

Table 2. Effect of niobium concentration on compressive properties of Cr-Nb binary alloys

Alloy number	Niobium concentration (at. %)	Strength (MPa)		Ductility (%)
		Yield	Tensile	
CN-7 ^(a)	6	866	1830	9.6
CN-4 ^(b)	12	960	1760	5.4
CN-45 ^(b)	17	1340	1340	~0

^(a)Annealed 5 d/900°C. ^(b)Annealed 3 d/1100°C.

MICROSTRUCTURE AND PHASE COMPOSITION IN CN ALLOYS

The CN alloys basically contain two phases, i.e., the Cr_2Nb intermetallic phase and the chromium-rich solid solution (which contains up to 6 at. % Nb at the eutectic temperature of 1620°C).⁵ In the as-cast condition, the CN alloys exhibit patches of the supersaturated chromium-rich phase surrounded by the eutectic structure $\text{Cr}_2\text{Nb}+\text{Cr}(\text{Nb})$. The supersaturated chromium-rich phase precipitates out fine Cr_2Nb particles when being annealed for 3 to 5 days at 900 to 1200°C, and a uniform distribution of fine Cr_2Nb particles is achieved by annealing at 1100°C (see Fig. 1).

Fig. 1. Backscattered electron image of (a) CN-43 (3,000x) and CN-52 (2,000x) specimens annealed for 3d at 1100°C.

The composition of the phases in the alloys CN-43, CN-52 and CN-53 was determined by electron microprobe analyses. Figure 1 shows the backscattered electron image of the alloy specimens annealed for 3 d at 1100°C. In this condition, the phase with a dark gray contrast is the Cr_2Nb phase. The precipitation of fine Cr_2Nb particles is visible within chromium-rich solid solution in these alloys. Table 3 summarizes the composition of the phases determined by wavelength-dispersive spectrometry (WDS). The chromium-rich solid solution (the matrix phase) contains low levels of niobium, 2.9 to 3.4% in CN-43 and -52 containing rhenium and 1% in CN-53 containing iron and nickel. The Cr_2Nb phase, on the other hand, contains 30.3-32.6% Nb in CN-43 and -52 and 27.8 Nb in CN-53. Surprisingly, iron and nickel partition strongly in the Cr_2Nb phase, instead of the chromium-rich solid solution, and they appear to occupy equally the chromium and niobium sublattice sites in the Cr_2Nb phase. The partitioning ratio of nickel and iron in the Cr_2Nb phase to the chromium-rich phase is 14 to 1 and 4 to 1, respectively.

Table 3. WDS compositional analysis of the CN alloys CN-43, -52 and -53

Alloy	Cr_2Nb -type phase (at. %)	Cr-rich phase (at. %)
CN-43 ^a	Cr=64.7	93.9
	Nb=30.1	3.4
	Re=3.3	1.3
	Al=1.9	1.4
CN-52	Cr=63.7	94.1
	Nb=32.6	2.9
	Re=2.1	2.1
	Al=1.6	0.9
	Hf=0.01	0.03
CN-53	Cr=56.4	96.6
	Nb=27.8	1.0
	Fe=5.2	1.2
	Ni=8.2	0.6
	Al=2.4	0.6
	Hf=0.03	0.05

^aThe yttrium concentration in the alloy was not analyzed

Aluminum and rhenium are moderately enriched in the Cr_2Nb -type phase. These results suggest that the Cr_2Nb phase is able to dissolve extensive amounts of solutes in the CN alloys.

Precipitation of the Cr_2Nb phase from the chromium-rich matrix is very sluggish. Cr_2Nb precipitates in the CN alloys are extremely fine, with a size of $\sim 0.3 \mu\text{m}$ for alloy specimens annealed for 3 d at 1100°C . This suggests a slow diffusion of niobium and low interfacial energy of Cr_2Nb particles. Microporosity is observed in the CN alloys, with a porosity size typically less than $20 \mu\text{m}$.

Both as-cast CN-43 specimens and specimens annealed for 5 d at 900°C plus 3 d at 1200°C were examined by TEM. Specimens were cut into 3 mm disks by EDM and hand ground to a thickness of approximately $50 \mu\text{m}$. Ion milling at 6 kV was used since the two phase materials could not be successfully electropolished. Specimens were examined in a Philips CM30 at 300 kV. Energy dispersive spectroscopy (EDS) was performed in a Philips CM12 at 120 kV with an EDAX 9100 spectrometer. The EDS analysis was made on precipitates that intersected ion milling perforations, thereby minimizing the contribution from surrounding material.

Specimens of as-cast CN-43 showed chromium-rich solid-solution patches surrounded by an eutectic structure. The Cr_2Nb phase is darker in the micrographs shown in Fig. 2(a). The white areas are multiple perforations in the film resulting from ion milling. In the as-cast specimens, no further precipitation was noted. The Cr_2Nb phase was extensively internally twinned, an example is shown in Fig. 2(b). The microtwinning has been observed in other Laves phases.^{6,10} Dislocation pileups were observed in the matrix impinging on the eutectic phase.

After an anneal for 5 d at 900°C plus 3 d at 1200°C , specimens of CN-43 were found to have an extensive secondary precipitation of the Cr_2Nb phase [Fig. 3(a)]. The precipitates were about $0.7 \mu\text{m}$ in diameter. No dislocations were observed in this material. These secondary precipitates were also internally twinned [Fig. 3 (b)].

The results of EDS analysis of these two specimens are given in Table 4. The spectrums were collected from where each phase intersected the ion-milling perforations and so little interference from the neighboring phase occurred. In the as-cast material, the eutectic phase is close to the expected composition of Cr_2Nb . The rhenium and aluminum additions are fairly evenly distributed between the chromium-rich matrix and the eutectic phase. The yttrium additions are too low to be observed by this technique. The matrix is

Fig. 2. TEM micrographs of as-cast CN-43 showing (a) chromium-rich patches surrounded by the eutectic structure and (b) a higher magnification micrograph showing the twinned structure in the Cr₂Nb phase and the dislocation pileups next to the precipitates.

Fig. 3. TEM micrographs of CN-43 after an anneal for 5 d at 900°C and 3 d at 1200°C showing (a) Cr₂Nb precipitates in the chromium-rich patches surrounded by the eutectic structure and (b) a higher magnification micrograph of the internal twinning in the 0.7 μm Cr₂Nb precipitates.

enriched in chromium and depleted in niobium. After the anneal, both the large eutectic phase and the secondary precipitation were moderately enriched in both aluminum and rhenium. Furthermore, most of the remaining niobium has precipitated into these secondary precipitates. After the anneal, the matrix contained about 95% Cr. These results agree well with those from the electron-microprobe analyses.

Table 4. EDS/TEM compositional analysis of CN-43 (at. %)

	Al	Nb	Cr	Re
<u>As Cast</u>				
Cr-rich phase	4	5.5	85.5	5
Large Cr ₂ Nb phase	5.5	29	62	3.5
<u>Annealed</u>				
Cr-rich phase	2	1	95	2
Large Cr ₂ Nb phase	3.5	28	63.5	5
Small precipitates	6	29	60	5
<u>Nominal</u> (plus 0.04 wt % Y)	2	12	82	4

MECHANICAL PROPERTIES OF CN ALLOYS

Mechanical properties of CN alloys were determined essentially by compression testing at room temperature, 1000°C and 1200-1500°C. Alloy specimens were annealed for 3 d at 1100°C prior to testing at room temperature in air and at elevated temperatures in vacuum. Table 5 summarizes the compressive properties of CN alloys containing Re, Al, Ni and Co. For the alloys with 12% Nb, the yield strength increases and the ductility decreases with alloy additions at room temperature. At 1000°C, rhenium increases the yield strength whereas other elements decrease the strength. Alloying with ≥8% Al, Ni and Co lowers the ductility at 1000°C. The 12% Nb alloy CN-44 maintains an excellent strength even at 1250°C. For the alloys containing 5.6-6.0% Nb, the room temperature yield strength is slightly lowered, and the ductility is increased by alloying additions. At 1000°C, rhenium is the element which improves the yield strength and ductility of the 6% Nb alloy whereas other elements lower the strength. At 1200°C, CN-52 containing 4% Re is substantially stronger than CN-53 with 2% Ni and Fe. Based on the compressive results, we conclude that rhenium is effective in improving the mechanical properties of the Cr-Nb alloys.

Table 5. Compressive properties of CN alloys
(alloy specimens were annealed for 3 d at 1100°C)

Alloy number	Concentration of key alloy elements (at. %)	Strength (MPa)		Ductility (%)
		Yield	Tensile	
<u>Room Temperature (Air)</u>				
CN-4	12Nb	960	1760	5.4
CN-44	12Nb-4Re-2Al	1230	2050	4.3
CN-46	12Nb-8Al	1090	1540	1.8
CN-49	12Nb-8Ni	1060	1610	2.9
CN-50	12Nb-12Ni	1250	1750	2.8
CN-56	12Nb-4Re-10Co	1460	1870	2.3
CN-7	6.0Nb	866	1830	9.6
CN-52	5.6Nb-4Re-1.5Al	754	1820	> 10.1 ^b
CN-53	5.6Nb-2Ni-2Fe	749	1660	> 11.6 ^b
<u>1000°C (Vacuum)</u>				
CN-4 ^a	12Nb	723	978	> 28 ^b
CN-44	12Nb-4Re-2Al	855	1061	> 26.2 ^b
CN-46	12Nb-8Al	616	980	11.3
CN-49	12Nb-8Ni	601	682	15.6
CN-50	12Nb-12Ni	502	636	15.9
CN-56	12Nb-4Re-10Co	527	948	5.8
CN-7	6.0Nb	499	666	14.2
CN-52	5.6Nb-4Re-1.5Al	548	1435	34
CN-53	5.6Nb-2Ni-2Fe	313	979	< 43
<u>1200-1250°C (Vacuum)</u>				
CN-4	12Nb	--	--	--
CN-44	12Nb-4Re-2Al	432	565	> 5 ^b
CN-7	6.0Nb	--	--	--
CN-52	5.6Nb-4Re-1.5Al	318	495	> 29 ^b
CN-53	5.6Nb-2Ni-2Fe	188	276	29

^aSpecimen was annealed for 4 d at 1000°C and 5 d at 900°C.

^bThe tests were stopped at the indicated strain.

An attempt was made to determine the tensile properties of the 12% Nb alloys containing rhenium and aluminum. Button-type alloy specimens were prepared by grinding, followed by annealing at 900-1200°C. The specimens fractured prior to macroscopic yielding, with a fracture strength of about 200 MPa. The poor fracture resistance is attributed to both cast porosity and coarse Cr₂Nb particles and platelets existing in the eutectic structure.

The creep properties of the CN alloys were determined by compression tests at 1000°C in vacuum under a stress of 345 MPa (50 ksi). The results are shown in Table 6 for the alloys CN-44, -52 and -53. In terms of time for 15% creep strain, the alloy CN-44 containing 12% Nb is the strongest. The time for 15% strain is 800 min for CN-52 and only 18 min for CN-53, indicating that alloying with 4% Re dramatically improves the creep resistance of the 5.6% Nb alloy. This comparison indicates that the creep resistance of the CN alloys depends on both niobium concentration and alloying element, and that the creep properties can be effectively improved by alloying additions such as rhenium.

Table 6. Creep properties of CN alloys tested at 1000°C at 345 MPa (50 ksi)

Alloy number	Nb concentration (%)	Time (min) for 15% creep strain
CN-44	12.0	2,400
CN-52	5.6	800
CN-53	5.6	18

SUMMARY AND FUTURE WORK

Microstructure and mechanical properties of CN alloys containing 5.6 to 17 at. % Nb were studied for high-temperature structural applications. The alloys generally contain two phases: one is the Cr₂Nb intermetallic phase and the other is the chromium-rich solid solution. In the as-cast condition, the alloys show chromium-rich patches surrounded by the eutectic structure Cr₂Nb+Cr(Nb), the amount of which decreases with decreasing niobium concentration. The supersaturated chromium-rich patches (containing ~6 at. % Nb) precipitated out fine Cr₂Nb particles (<1 μm) in alloys annealed at 900-1200°C.

Alloying elements of Re, Al, Ni and Co at levels to 30 at. % were added to Cr-Nb alloys. Compositional analyses by EDS/TEM and WDS/electron microprobe indicate that nickel and iron are strongly enriched in the Cr₂Nb phase and depleted in the chromium-rich solid solution. Aluminum and rhenium are, on the other hand, enriched moderately in the

Cr₂Nb phase. These results indicate that the intermetallic phase is able to dissolve extensive amounts of solutes in the CN alloys.

Mechanical properties of the CN alloys were determined at temperatures to 1250°C. The yield strength increases and the compressive ductility decreases with increasing niobium concentration. Among the alloying elements, rhenium is most effective in improving the mechanical properties at room and elevated temperatures. Alloying with ≥8% Al, Ni, and Co appear to lower the strength and ductility at elevated temperatures, such as 1000°C. The creep resistance of the CN alloys depends on both niobium concentration and alloy additions. Creep tests at 1000°C and 345 MPa indicates that rhenium is beneficial and nickel and iron are detrimental to the creep properties of the 5.6% Nb alloys.

The 12% Nb alloy showed poor fracture resistance in tension at room temperature. Future studies will be focused on improving tensile properties of the CN alloys by (1) control of microstructure by alloy addition and thermomechanical treatment, (2) reduction of cast defect using innovative processing techniques, and (3) adjustment of niobium concentration.

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2.6 DEVELOPMENT OF IRON ALUMINIDES

C. G. McKamey, S. Viswanathan, and V. K. Sikka

INTRODUCTION

Recent studies have demonstrated that improved engineering ductility (to 10-15% in Fe₃Al) can be achieved in wrought Fe₃Al-based iron aluminide alloys through control of composition and microstructure.¹⁻⁴ Accompanying this improvement has been an increased understanding of the causes for ambient temperature embrittlement in this system.⁵⁻⁶ Because of these advances, iron aluminide alloys are being considered for many structural uses, especially for applications where their excellent corrosion resistance is needed. Several alloy compositions developed at ORNL have been licensed to commercial vendors for development of scale-up procedures. With the licensees and other vendors, several applications for iron aluminides are being pursued.

The understanding and control of cast structures are important steps in making iron-aluminide alloys viable engineering materials. This includes understanding the various components of cast structure, their evolution, their properties, their behavior during further processing, and, finally, their effect on mechanical properties. The first phase of our study of cast Fe₃Al-based alloys characterized the various components of cast structure in the FA-129 alloy,^{7,8} while the current phase of the research involves characterizing the as-cast mechanical properties of Fe₃Al-based alloys. In this reporting period, room-temperature tensile properties of as-cast Fe₃Al, Fe₃Al with chromium, and the FA-129 alloy were investigated. Tensile properties in the as-cast condition were correlated with the microstructure and fracture morphology, and some observations were made regarding tensile properties. Room-temperature tensile properties of FA-129 alloy were also investigated after homogenization at 700, 900, and 1200°C.

DISCUSSION OF CURRENT ACTIVITIES

Tensile Properties of As-cast Iron-Aluminide Alloys

Vacuum-induction melts of binary Fe₃Al, Fe₃Al with chromium (Fe-28% Al-5% Cr), and FA-129 alloy (Fe-28% Al-5% Cr-0.5% Nb-0.2% C) were prepared (all compositions indicated are in atomic percent and refer to nominal compositions) and cast in a graphite mold of dimensions 2.5 × 15 × 10 cm (see Fig. 1). The ingots were examined

Figure 1. Schematic of the graphite mold used to cast Fe_3Al -based alloys.

radiographically to ensure that they were free from macroscopic shrinkage. It was intended that standard tensile test specimens (1.28 cm diam, 5 cm gauge length) would be used due to the relatively large grain size of cast alloys and the desire to have a reasonable number of grains within the test-specimen cross section. However, the actual specimens used were somewhat smaller (1.0 cm diam, 5 cm gauge length) in order to stay within the load capacities of the test machines used. Four tensile specimens were obtained from each ingot. For each alloy, two specimens were tested in air, and two specimens were tested under a vacuum of 2.7×10^{-5} Pa. A screw-driven Instron test machine was used for tests in air while a servo-hydraulic test machine (primarily used for fatigue tests) was used for the vacuum tests, as a screw-driven machine equipped with a vacuum chamber was not available. A second ingot of FA-129 alloy was prepared for homogenization tests. Due to the relatively fine grain of FA-129 alloy, it was decided that all further tests on FA-129 alloy would use smaller test specimens to allow a larger number of test specimens to be obtained from each ingot. Six coupons (1.3 cm diam, 9 cm long) were obtained from the ingot. Two coupons each were homogenized at 700, 900, and 1200°C for 1 h and air-cooled, and undersized tensile specimens (0.64 cm diam, 2.5 cm gauge length) were machined from the coupons. All tensile tests were conducted at room temperature and at a strain rate of 0.003 s^{-1} .

Tensile specimens were characterized by visual observation, by observation of the specimen and fracture surface under a low-power stereo microscope, and by scanning electron microscopy (SEM). In addition, samples were examined by transmission electron microscopy (TEM) in order to determine the type and extent of ordered phase.

Figure 2 compares tensile properties for tests conducted in air and in vacuum. For tests conducted in air, strength values were slightly higher for the binary and FA-129 alloys than the ternary alloy with chromium. Correspondingly, total elongation values were highest for the ternary alloy, almost 3%, while those for the binary and FA-129 alloys ranged from 1 to 1.5%. The results follow the same general trend as for wrought material⁹ and suggest that the addition of chromium served to soften the material, although both the strength and ductility obtained in the cast condition were considerably lower than values in the wrought condition. In addition, all specimens exhibited extensive cracking along the gauge length. Cracks appeared to be intergranular and were perpendicular to the specimen axis. The contribution of crack separation to the total elongation was not quantified, although visual observation indicated that it could be significant, suggesting that the true ductility was lower than the measured total elongation values.

Unlike tests in air, strength values for tests in vacuum showed little variation with alloying. Also, although strengths were lower for tests conducted in air, total elongation values were actually the same or higher for tests conducted in air compared to tests in vacuum. This is in contrast to wrought materials, where higher total elongations are obtained in tests conducted in vacuum, indicating an environmental effect.¹⁰ It is not clear whether the difference in behavior in the cast material was due to the difference in testing machines used for tests in air and in vacuum, or whether the extremely low ductility of the cast material masked effects due to environment. Similar to tests in air, specimens tested in vacuum also exhibited extensive cracking along the gauge length. The extent of cracking also appeared to be similar.

Samples tested in both air and in vacuum exhibited almost identical fracture morphologies, consistent with the very similar tensile properties obtained in air and vacuum. As indicated earlier, all of the samples had intergranular cracks perpendicular to the loading direction. The size of the cracks correlated directly with the grain size. The largest cracks were found in the ternary alloy with chromium, which also exhibited the largest grain size, almost 2 mm. The FA-129 alloy had the finest cracks and exhibited the finest grain size,

Figure 2. Room temperature tensile properties in air and vacuum for the binary Fe_3Al alloy, the ternary Fe_3Al with chromium, and FA-129 alloy. Strain rate was 0.003 s^{-1} .

about 0.5 mm. The binary alloy exhibited a grain size of about 1 mm. In all cases, grains were equiaxed. However, in the case of the binary and ternary alloys, the as-cast grain

boundaries were no longer evident in the microstructure and had been replaced by grains formed during the transformation to the $D0_3$ ordered phase.

The examination of the fracture surface revealed that the fracture mode in the binary alloy was almost completely intergranular. The fracture mode of the ternary alloy with chromium was almost completely transgranular, while the FA-129 alloy exhibited a predominantly transgranular mode of fracture with about 30% intergranular failure. Figure 3 shows typical fracture morphologies obtained in the three alloys. All alloys exhibited some microporosity, as would be expected with cast microstructures. The pore and fracture surfaces of the binary alloy were relatively clean, but the pores of the ternary alloy exhibited unidentified deposits that may be chromium carbides. The pore surfaces of the FA-129 alloy also exhibited some unidentified deposits and large quantities of precipitates in the interdendritic regions. The interdendritic phase in the FA-129 alloy has previously been identified as niobium carbide.⁸ The intergranular fracture surfaces of the FA-129 alloy exhibited unidentified features that took on the appearance of "chicken tracks" at lower magnification. Further work is presently in progress on identifying microstructural features. Figure 4 shows typical microporosity and microstructural features found in the fracture surfaces of the three alloys.

TEM analysis of tensile specimens indicated that the matrix phase in all of the alloys was $D0_3$. Very few dislocations were found in the matrices of the as-cast alloys, although some regions of high dislocation density were detected around niobium carbide precipitates in the FA-129 alloy. In general, results were very similar to those found previously for the FA-129 alloy.⁷

Figure 5 shows tensile properties for samples homogenized at 700, 900, and 1200°C for 1 h. The yield strength increased with homogenization temperature, possibly due to niobium going into solution. Ultimate tensile strength and total elongation exhibited a maximum at a homogenization temperature of 900°C. Interestingly, total elongation was 3% for the sample homogenized at 900°C, almost twice the total elongation obtained in the as-cast condition. Also, samples seemed to exhibit fewer cracks perpendicular to the loading direction compared to the as-cast samples. Microstructural characterization of the samples is in progress.

The low ductility of as-cast Fe_3Al -based alloys may be related to the relatively large grain size in the cast condition, the low dislocation density in as-cast samples, and the

Figure 3. Scanning electron fractographs showing typical fracture morphologies for: (a) binary Fe_3Al , (b) Fe_3Al with chromium, and (c) alloy FA-129.

Figure 4. Scanning electron fractographs showing typical features of the fracture surfaces: (a) shrinkage porosity in binary Fe_3Al , (b) solidification steps in binary Fe_3Al , and (c) gas porosity in Fe_3Al with chromium.

Figure 4 (cont.) Scanning electron fractographs showing typical features of the fracture surfaces: (d) "chicken tracks" on intergranular faces in FA-129, (e) shrinkage porosity in FA-129, and (f) molten carbide dendrite formation in FA-129.

Figure 5. Room temperature tensile properties for alloy FA-129 homogenized at 700, 900, and 1200°C for 1 h. Tests were conducted in air at a strain rate of 0.003 s^{-1} .

presence of the D0_3 ordered phase. Homogenized samples of FA-129 alloy exhibited almost twice the ductility of the as-cast condition. Microstructural characterization of the

homogenized samples and comparison of the as-cast and homogenized microstructures may provide a clue to the poor ductility in the as-cast state.

Commercialization Status of ORNL Alloys

Several alloy compositions developed at ORNL and licensed to commercial vendors for manufacturing are listed in Table I. The licensees are (1) Ametek Specialty Metal Products Division for powder production, (2) Hoskins Manufacturing Co. and (3) Harrison Alloys for production of heating elements, and (4) Cast Masters for production of cast parts. These and other vendors have produced various sizes of pilot heats, including heats of 2000 and 3000 kg melted by Precision Rolled Products.^{11,12}

With these companies and others, several specific applications are being pursued,¹³ all of which will result in reduced cost and lower use of strategic elements. These include:

1. Heating elements for toasters, stoves, ovens, cigarette lighters, and dryers, where the iron aluminide will replace Nichrome wire. For this application Fe_3Al has the advantages of improved oxidation resistance and significantly superior thermal cycling resistance.

2. High-temperature insulation wrapping wire for investment-casting molds. The wire needs to operate reliably at temperatures up to 1100°C in holding the insulation

Table I. Nominal compositions of iron aluminide alloys currently being commercialized.

Element	Nominal composition (at. %)				
	FAS ^a	FAL ^b	FA-129 ^c	FAP ^d	FAPY ^d
Al	28.08	28.03	28.08	16.12	16.12
Cr	2.02	5.03	5.04	5.44	5.44
B	0.04	0.04			
Zr		0.08		0.11	0.11
Nb			0.51		
C			0.20	0.13	0.13
Mo				1.07	1.07
Y					0.06
Fe	69.86	66.81	66.17	77.13	77.07
^a Good sulfidation resistance. ^b Good RT tensile ductility. ^c High-temperature tensile strength with good RT ductility. ^d High RT ductility.					

wrapped around the mold. Fe_3Al will replace the stainless steel wire currently used and should result in a lower rejection rate of investment-cast parts because of its improved oxidation resistance and longer life.

3. Regenerator discs in automotive gas-turbine engines. Discs are used to recover heat from the hot gases of gas-turbine engines in buses and trucks. This application will replace a nickel alloy containing cobalt and offers the advantages of reduced engine weight and longer life.

4. Hot-gas filters in the coal-gasification process. These filters are used to trap the particulate matter from the gas produced in the coal-gasification process. The sulfidation resistance of the iron aluminides is superior to currently used ceramics and highly-alloyed metals and will result in longer life and enhanced reliability.

5. Dies for superplastic forming of titanium-based alloys. The presence of nickel in the conventional die materials embrittles the titanium-based alloys. Iron aluminides will replace the nickel-base alloys and will provide better oxidation resistance, lower die cost, and longer life, and will result in improved quality of superplastically-formed parts.

6. Shields for protecting superheater tubing from oxidation and erosion in coal-fired power plants. The currently-used stainless steel shields must be replaced every two years. Iron aluminides will provide lower cost, longer life, and reduced down time to replace shields.

7. Exhaust manifolds, catalytic converters, mufflers, and exhaust support hangers for automotive applications. The iron aluminides will replace ceramics in the catalytic converters and the 400 series iron-chrome steels in the other applications. For these applications, they offer better oxidation and aqueous corrosion resistance, lighter weight with improved energy efficiency, longer component life, and lower cost.

8. Other applications such as sensors in molten metal processing systems, nickel-free alloy jewelry, and structural uses in highly oxidizing salts (such as nitrates) are being considered.

Additional work is needed to improve the ductility and strength of Fe_3Al -based alloys in both the as-cast and wrought conditions. Also, efforts are needed to develop welding wire, coated electrodes, and fluxes for welding procedures. A data base of physical and mechanical property data needs to be generated on those alloys being produced commercially and on the high-strength alloys currently being developed.

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2.7 MICROALLOYED IRON ALUMINIDES

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INTRODUCTION

Development efforts at this laboratory have indicated that by controlling alloy chemistry and thermomechanical processing, environmental embrittlement of Fe₃Al-based alloys can be minimized.¹⁻³ Ambient temperature tensile ductilities of 10-20% and tensile yield strengths as high as 500 MPa can be achieved in alloy FA-129 (Fe-28Al-5Cr-0.5Nb-0.2C, at.%).²⁻³ However, the tensile strength of Fe₃Al-based alloys decreases dramatically above 600°C and creep-rupture strengths of the FA-129 type iron aluminides at temperatures of 550°C and above remain unsatisfactory.⁴ Additions of elements such as Ti, Mo, Zr, Hf, and Nb can improve high temperature strength, but at the expense of room temperature ductility.^{1,5}

Welding is another major area of concern in the development of iron-aluminide alloys for structural applications. The welding processes used must be capable of producing high quality weldments under field and shop conditions which are free of defects and have mechanical properties comparable to the base metal. Initial work on the weldability of iron aluminides has identified a propensity for cold-cracking and a possible degradation of the mechanical properties of the weldment in comparison to the base metal.^{6,7} Weldability of alloy FA-129 has been greatly improved by optimizing the welding process and parameters (e.g., using pre- and post-weld heat treatments).⁷ Studies have also shown that the weldability of iron aluminides is very sensitive to minor changes in composition of the base metal.^{7,8}

The objective of this task is to use macro- and microalloying techniques on alloy FA-129 to produce an Fe₃Al-based alloy with improved creep-rupture resistance and tensile strength to temperatures as high as 700°C. At the same time, the alloy should have adequate room temperature tensile ductility (>10%), good weldability and fabricability, and maintain the excellent corrosion resistance identified with iron aluminides. The scope of this task will include studying alloying effects on creep-rupture strength, high-temperature tensile strength, and weldability, and identifying positive and negative synergisms, which

appear to play very important roles in all properties of this alloy system. This work is being coordinated with related efforts sponsored by the AIC Materials Program.

DISCUSSION OF CURRENT ACTIVITIES

During this reporting period, five new alloy compositions, along with a second ingot of two previous alloys, were prepared as 500-g ingots by melting and drop-casting into chilled copper molds. Fabrication to 0.76-mm-thick sheet was accomplished by first forging 50% in two steps at 1000°C (to 15 mm thickness), then hot rolling at 800°C to 2.5 mm thickness and warm rolling at 650°C to the final thickness. After a stress relief heat treatment of 1 h at 700°C, flat tensile specimens (0.76 × 3.18 × 12.7 mm) were mechanically punched from the rolled sheet and were further annealed for 1 h at 750°C. Tensile tests were conducted at room temperature and 600°C in air at a strain rate of $3.3 \times 10^{-3} \text{ s}^{-1}$. Creep-rupture tests were conducted in air at 593°C and 207 MPa.

Table I shows the compositions produced in this reporting period, designated as FA-179 through -184. These compositions were chosen to further study the effect of the niobium/molybdenum ratio on the properties. Also, one alloy was produced to see if hafnium substituted for zirconium would improve the weldability. Alloy compositions FA-168 and -176, which previously had shown good combinations of strength, ductility, and/or weldability properties, were remelted into ingots designated with a "B" and tested along with the new alloys. Table I shows the tensile properties at room temperature and 600°C; Table II shows the creep-rupture properties at 593°C and 207 MPa and the weldability as indicated by measuring the threshold cracking stress (TCS) needed to produce hot-cracking during welding (Sigmajig test).¹¹

Table I shows that the same elements added for RT strength also produce improved tensile strength at 600°C. In particular, the table shows that the maximum strengths are obtained for alloy compositions which include at least 0.5% Nb and 0.6% Mo, in combination with a small amount of zirconium. The addition of hafnium instead of zirconium (alloy FA-182) resulted in increased room temperature tensile strength, but did not improve the high temperature strength, either in tension (Table I) or in creep-rupture (Table II).

Table I. Tensile properties of Fe₃Al-based compositions

Alloy ^a FA-	Nominal Composition (at.%)	RT ^b			600°C ^b		
		Strength ^c (MPa)		El. (%)	Strength ^c (MPa)		El. (%)
		YS	FS		YS	FS	
129	Fe-28Al-5Cr-0.5Nb-0.2C	384	930	16.9	417	520	38.3
	<u>Fe-28Al-5Cr-0.005B</u>						
168B	-0.5Nb-0.8Mo-0.05Zr-0.03C	699	958	10.7	599	621	34.7
176B	-0.5Nb-0.4Mo-0.025Zr-0.05C	569	929	11.8	536	546	41.3
179	-0.5Nb-0.6Mo-0.025Zr-0.05C	658	985	10.0	554	565	33.8
180	-0.5Nb-0.8Mo-0.025Zr-0.05C	610	900	8.4	538	571	34.7
182	-0.5Nb-0.4Mo-0.025Hf-0.05C	626	975	10.9	546	566	41.2
183	-0.3Nb-0.8Mo-0.025Zr-0.05C	585	893	9.2	442	476	51.8
184	-0.1Nb-0.8Mo-0.025Zr-0.05C	435	705	7.0	430	462	52.2
^a Except where noted, all alloys were heat treated 1h at 700°C before punching specimens, then specimens were annealed for 1 h at 750°C. ^b Tested in air at a strain rate of 3.3×10^{-3} /s. ^c YS=0.2% yield strength, FS=fracture strength.							

Table II. Creep-rupture at 593°C and 207 MPa and hot-crack susceptibility as measured by the Sigmajig test for Fe₃Al-based alloys.

Alloy FA-	Nominal composition (at.%)	Creep properties			TCS ^a [MPa (ksi)]
		Life (h)	Elongation (%)	MCR (%/h)	
129	Fe-28Al-5Cr-0.5Nb-0.2C	16.8	68.9	1.5	=172 (25)
	<u>Fe-28Al-5Cr-0.005B</u>				
168B	-0.5Nb-0.8Mo-0.05Zr-0.03C	130.8	69.9	0.2	<<138 (20)
176B	-0.5Nb-0.4Mo-0.025Zr-0.05C	62.2	62.0	0.4	103-138 (15-20)
179	-0.5Nb-0.6Mo-0.025Zr-0.05C	119.5	72.9	0.2	131 (19)
180	-0.5Nb-0.8Mo-0.025Zr-0.05C	97.1	76.8	0.3	124 (18)
182	-0.5Nb-0.4Mo-0.025Hf-0.05C	78.6	59.8	0.4	131 (19)
183	-0.3Nb-0.8Mo-0.025Zr-0.05C	41.2	58.6	0.8	<96 (14)
184	-0.1Nb-0.8Mo-0.025Zr-0.05C	19.0	65.0	1.7	>138 (20)
^a Threshold cracking stress for initiation of hot-cracking during gas-tungsten-arc welding.					

The Sigmajig test was used as a means of comparing the weldability of the iron aluminides.⁹ This test uses a preapplied transverse stress during autogenous gas tungsten arc welding of a 50 by 50 mm sheet specimen to determine the threshold cracking stress (TCS) above which hot-cracking is initiated in the fusion zone during welding. Using this test, the weldability of FA-129 was determined to be better than nickel aluminides and comparable to several other commonly-used alloys. Its weldability has been improved still further by optimizing the welding process and parameters (e.g., using pre- and post-weld heat treatments to prevent cold-cracking).¹⁰ As shown in Table II, the alloying additions used to improve mechanical properties have resulted in slightly reduced weldability (as well as lower room temperature tensile ductility, Table I). By controlling the ratio of Nb, Mo, and Zr, and adding a small amount of carbon to enhance weldability, it is now possible to produce an acceptable balance of strength, ductility, and weldability properties (for example, see properties of alloys FA-179 and -180 in Tables I and II). However, the amount of carbon added is critical; although it appears to enhance weldability, too much results in dramatic decreases in high-temperature creep resistance.¹¹

Table III summarizes the results of EDAX analyses of hot crack surfaces of two heats of Fe₃Al in the scanning electron microscope. The analysis of the cold cracking surface of FA-180 should give essentially the nominal alloy composition, since the fracture is transgranular. The hot crack surface represents the last liquid to solidify, and can sometimes point to elements involved in the hot cracking process. Niobium is seen to be enriched on the hot crack surface for both FA-180 and FA-168, which had widely varying cracking sensitivity. Aluminum also appears to be somewhat increased. Zirconium was

Table III. EDAX Analysis of Fe₃Al Fracture Surfaces

Fe ₃ Al heat		Composition (wt.%)			
		Al	Cr	Mo	Nb
FA-180	Nominal	16.0	5.4	1.6	1.0
	Cold crack	15.2	5.6	1.4	0.6
	Hot crack	18.9	4.7	2.6	4.2
FA-168	Nominal	16.0	5.4	1.6	1.0
	Hot crack (1)	18.2	5.2	1.4	2.2
	Hot crack (2)	21.6	4.6	1.8	2.6

below the EDAX detectable limit and this particular equipment/technique is unable to detect boron and carbon. The detailed mechanism for hot cracking in these alloys is thus still to be determined, although progress has been made toward elucidating the effect of some elements, and compositions have been developed which have hot cracking resistance equivalent to commercial austenitic stainless steels.

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

R.W. Swindeman

ABSTRACT

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

INTRODUCTION

Research on austenitic alloys for advanced steam cycle applications was begun six years ago in support of a research effort by the Electric Power Research Institute (EPRI) to improve performance of pulverized coal power plants (1). The initial thrust at ORNL was to evaluate austenitic alloys that could be used for superheater tubing in the EPRI Phase 2 conceptual plant. The target was an alloy for the production of steam at 650°C and 35 MPa. The EPRI Phase 2 effort received very little support by the U.S. utility industry. Interest continued in the EPRI Phase 1 conceptual plant, however, and several advanced alloys that EPRI helped to develop for this application in Japan are approaching Code status in the U.S. These materials included Sumitomo HR3C stainless steel, Nippon steel NF 709, and Nippon Steel NF 616. When Code approved, these alloys will be available for use in plant life extension and re-powering. State-of-the-art combined cycle concepts and

second generation combined cycle concepts received attention from the DOE energy technology centers as well as from EPRI, utilities, and industry in the U.S. Europe, and Japan. Recognizing that issues remain regarding the use of new materials for re-powering and combined cycle concepts, the work described below represents the efforts undertaken in the last year to collaborate with the fossil power industry in various areas of structural materials technology. Topics that are covered include plant life extension, increase of steam temperatures to 600°C, hot-gas cleanup for pressured fluidized bed combustors, and structural alloys for second generation combined cycle applications.

PLANT LIFE EXTENSION

One effort on plant life extension involved the continuation of stress-rupture tests on type 316N stainless steel and CRE 16-8-2 weld metal for joining high-strength austenitic stainless steels used in main steam line piping. This work was begun as a collaborative effort with South Carolina Gas and Electric Company and Tordonato Energy Consultants, Inc. and testing has continued to beyond 20,000 h with excellent strength and ductility being observed in 316N stainless steel that had been in service at 540°C for approximately 95,000 h (2). See Fig. 1.

Fig. 1. Creep curves for type 316N stainless steel removed from the main steam line piping of a fossil power plant after 95,000 h at 540°C.

Another effort on plant life extension involved the use of Gr-91 steel in superheaters and headers. Superheater tubing in the Tennessee Valley Authority (TVA) Kingston Steam Plant Unit 5 was inspected after 10 years of operation. The tubing was found to be in excellent condition. Stress rupture data on aged Gr-91 steel were evaluated, and a simple rule for prediction of creep response after aging was developed (3). Working with Tordonato Energy Consultants, Inc., a model was developed for the prediction of tertiary creep response in Gr-91 steel (4). See Fig. 2. Additional testing of Gr-91 was undertaken to assist in the evaluation of a tube failure due to a temperature excursion in a power boiler.

Creep Strain Versus Time For Grade 91 Heat 30383;593C and 110MPa

Fig. 2. Comparison of long time creep curves for Gr-91 with a model developed by Ellis and Swindeman to include tertiary creep.

ADVANCED STEAM CYCLE

Research was undertaken to support the advanced steam cycle goal of producing steam at 600°C. The influence of thermal mechanical treatment on the strength and ductility of the modified alloy 800H was examined for times approaching 20,000 h and for temperatures to 730°C. The modified 800H alloy was found to be tolerant of cold work to levels of 15% without loss of strength due to recrystallization. See Fig. 3. Weld metals

such as CRE 16-8-2 stainless steel and alloy 556 continued to exhibit good properties after testing times exceeding 20,000 h.

Fig. 3. Influence of cold work on the rupture strength of modified alloy 800 tested at temperatures in the range of 600 to 760°C.

A significant effort continued on the performance of Gr-91 in advanced steam cycle applications. Stress rupture data from around the world have been collected and re-evaluated for service to 600°C and higher. Additional testing was performed to examine techniques for extrapolation of data. Techniques included time-temperature parametric procedures, isostress testing, and Monkman Grant analyses (5). This collaborative effort involved German and Japanese researchers, and the combined stress-rupture data are shown in Fig. 4. The log stress is plotted against the Dorn parameter for more than 800 tests. Overall, the trend of the data indicated that the original stress values proposed for temperatures in the range of 575 to 650°C were adequate. The European steels tended to be somewhat weaker than the U.S. and Japanese steels, and some adjustment of design stresses may be forthcoming. To accommodate the loss in strength due to long time aging a model was developed that correlated life with aging time (5). This model is being tested with a new set of tests on aged materials. An effort has been started to collaborate with a major U.S. utility, a boiler manufacturer, and a university to examine the performance of Gr-91 thick-section weldments in a header vessel for service to 610°C. The material is the first commercial heat of Gr-91 melted in the U.S. in more than ten years.

Fig. 4. Log stress versus the Dorn-Shepard parameter correlating life and temperature for stress rupture data on Gr-91 steel produced by U.S., Japanese, and German sources.

HOT-GAS CLEANUP

Materials and design methods for construction of structural components in hot-gas cleanup vessels for pressurized fluidized bed combustors (PFBC) are being evaluated. Coupons of several structural alloys (alloy 556, alloy 333, RA85H stainless steel, and 310HCbN stainless steel) were supplied to Westinghouse Electric Corporation for exposure in the Tidd Plant gas filter vessel (6). Creep and fatigue of materials such as RA-333 and alloy 556 is continuing at a relatively low level of effort. Alloy 556 was approved recently for construction under the rules of ASME Sect. VIII for temperature to 870°C. Because of the low yield strengths of commercially available high temperature structural alloys, they are susceptible to low-cycle fatigue failures under restrained thermal cycling conditions. A nickel-chrome-aluminide intermetallic alloy was selected as an alternative material for tube sheet construction because of its very high yield strength at 870°C. Cyclic testing of IC 396M was continued to produce a data base sufficient for elastic-plastic-creep analysis in structural applications in a collaborative effort with Mallett Software Technology, Inc. Under conditions of 50% restraint, virtually no inelastic strains occurred after the first transient in IC396M cycled between 150 and 835°C. After shakedown, thermal transients produce only elastic strains. A typical response curve is shown in Fig. 5.

Fig. 5. Stress versus strain response of intermetallic alloy IC396M during thermal cycles of 150 to 835°C with 50% restraint.

SECOND GENERATION COMBINED CYCLE

Materials and design methods for second generation combined cycle plants were examined. In a collaborative effort with Stress Engineering Services, Inc., criteria for design above 815°C were studied (5). The initial work was undertaken on alloy 800H to determine the degree of conservatism embedded in the existing criteria for design in the various Sections of the ASME Boiler and Pressure Vessel Code. Studies were extended to other Code alloys and candidate structural alloys. Of particular interest has been the shape of the creep curve at very high temperatures and the response to cyclic loading in the presence of aggressive environments. Alloy 333, 253MA stainless steel, and RA85H stainless steel were evaluated in collaboration with Rolled Alloys, Inc.

After consulting with several contractors involved in the design of second generation combined cycle system components, it became clear that many materials issues needed resolution. For PFBC gas streams, material selection for piping liners, expansion bellows, and filter supports were areas of importance. Type 310 stainless steel was a primary candidate on the basis of cost, but stronger alloys were sometimes needed. Carbonizers and gasifier gas streams presented greater problems because of the greater potential for sulfidation.

The potential of modified type 310 stainless steel for fossil energy applications at temperatures above 815°C (8) was assessed, and it was concluded that a 25Cr-20Ni steel having a strength comparable to alloy 800H would be of interest. Two commercial heats of 310HCbN stainless steel tubing were procured, annealed at 1200°C, and subjected to creep-rupture testing in the temperature range of 760 to 982°C. To date, both heats have exhibited good strength and ductility and were stronger than alloy 800H. One experimental heat of a Ta-modified 310 stainless steel was procured as an ingot. The ingot was hot rolled to 13-mm plate, annealed at 1200°C, and specimens were creep-rupture tested in the temperature range of 760 to 1038°C. The alloy was found to have excellent creep strength (Fig. 6). Exploratory testing in regard to cyclic oxidation resistance and weldability indicated favorable trends. Thus, lower cost alloys with improved strength may become available for use in non-sulfidizing environments.

Fig. 6. Comparison of the 1000 h rupture strength for several alloys over the temperature range of 650 to 1100°C.

For protection against coal-ash corrosion at temperatures above 760°C, exploratory testing of tubing clad with alloy 671 and alloy 690 was undertaken (8). Tube sections of alloy 800H clad with alloy 671 and modified alloy 800H clad with alloy 690 were subjected to cyclic oxidation testing to 900°C for 500 h. Each day the tubes were cooled to near room temperature. The purpose was to examine cyclic oxidation characteristics of the base metal and the character of the clad base metal interface. Both the 671/800 and the 690/mod800 clad interfaces exhibited no detrimental changes (Figs. 7 and 8), but the modified alloy 800 showed severe oxide attack on the unclad inside diameter. A bare 310HCbN stainless steel tube was subjected to similar cycling and, based on inspection of the surface, exhibited good oxidation resistance. Quantitative measurements of oxidation rates are being planned.

Fig. 7. Microstructure of the interface between alloy 671 cladding and alloy 800H after 500 h at 900°C with one thermal cycle to near room temperature each day.

Fig. 8. Microstructure of the interface between alloy 690 cladding and modified alloy 800H after 500 h at 900°C with one thermal cycle to near room temperature each day.

For protection against sulfidizing environments, the potential of iron-aluminide cladding is being explored. For carbonizer and gasifier gas streams operating to 900°C, the aluminide cladding on piping liners and internal vessel structural components is being considered. To examine the compatibility of the base metal and cladding, cyclic testing of aluminide clad 304 stainless steel tubing was undertaken. Testing was performed at 760 and 900°C for 500 h with a cool down to near room temperature each day. The clad base metal interface exhibited no detrimental changes, as shown in Fig. 9.

Fig. 9. Microstructure of the interface between iron aluminide cladding and 304 stainless steel after 500 h at 900°C with one thermal cycle to near room temperature each day.

SUMMARY

Progress has been made on the evaluation of structural materials for a number of fossil energy applications, and most of the research involves collaborative efforts with industry. The selection of materials and research thrusts were selected to meet the needs of industrial partners. Several issues regarding the use of Gr-91 steel in life extension and re-powering were addressed. Materials for construction of components in second generation combined cycle applications were examined, and emphasis was placed on gathering data needed for establishing design methods and analysis procedures.

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2.9 EFFECTS OF ALLOYING AND TEMPERATURE ON THE HIGH-TEMPERATURE OXIDATION OF Cr-Cr₂Nb

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INTRODUCTION

Chromium-based alloys incorporating the Cr₂Nb Laves-phase alloys are potential new materials for use in hostile environments of advanced heat engines and energy systems that operate at very high temperatures to achieve better energy efficiency.^{1,2} In compression, Cr-Cr₂Nb alloys have been shown to be substantially stronger than conventional nickel-based superalloys at high temperatures while exhibiting some ductility.¹ However, much more development is needed to overcome castability problems and low fracture toughness. In addition, high temperature oxidation behavior and scaling resistance of Cr-Nb alloys must be evaluated under a variety of relevant metallurgical and environmental conditions.

Previously-reported oxidation results³ showed that, upon air exposures at 900 and 950° C, binary Cr-Cr₂Nb alloys containing 6 and 12% Nb* developed multilayer scales with an outer layer of chromia and inner products containing niobium. Spallation and indirect evidence of isothermal scale cracking were observed. The alloy with the higher concentration of niobium showed better oxidation resistance in terms of weight gain and scale adherence. This was attributed to its greater volume fraction of the Cr₂Nb-Cr eutectic at the expense of the Cr-rich phase. Further studies have now been conducted to evaluate effects of selected alloying additions on the isothermal and cyclic oxidation resistance of Cr-Cr₂Nb alloys in air and to examine the corrosion process as a function of temperature (for binary Cr-12% Nb) in order to determine the upper limit for effective protection by thermally grown scales. Some of these results are reported in the present paper.

EXPERIMENTS PROCEDURES

Alloys of Cr-Nb were prepared by arc melting and drop casting into water-cooled copper molds. Table 1 lists the alloy compositions discussed in this paper. (See ref. 2 for

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*Compositional percentages denote at.%.

microstructural and mechanical characterization results for many of these compositions). Rectangular specimens (approximately 8 x 8-16 x 1 mm) were cut from the ingots by electrodischarge machining. All major surfaces were mechanically ground with 600-grit SiC abrasive before exposure.

Table 1. Nominal compositions of alloys used in this study.

Alloy (CN-)	Nb	Composition (at.%) ^(a) (Al)	Other
4	12		
4A	12	8	
7	6		
7A	6	8	
43 ^(b)	12	2	4 Re, 0.03Y
46 ^(b)	12	8	
47 ^(b)	12	12	
48 ^(b)	12	16	

^(a) Balance is Cr.

^(b) Higher purity: < 200 wt ppm of oxygen and carbon versus 700-1000 wt ppm for other alloys. (ref. 2)

For isothermal exposures, weight changes were measured using Cahn 1000 microbalances and a computer-controlled data acquisition system. The specimens were exposed to flowing, preheated, dried air (2 cc/s) at 1100°C for up to 180 h. At the end of each experiment, the specimens were furnace cooled and visually checked for loss of corrosion products by spallation. Thermal cycling experiments were conducted in horizontal tube furnaces at 950°C. Specimens were withdrawn at intervals of 24 - 72 h, cooled to room temperature, visually examined, weighed, and returned to the furnace. Selected specimens from both types of experiments were analyzed by optical imaging and by scanning electron microscopy (SEM).

RESULTS

The oxidation of the baseline binary alloy containing 12% Nb was studied over a temperature range of 900 to 1100°C. Thermogravimetric data from isothermal exposures to dry air at 900 and 1100°C are shown in Fig. 1, which also includes previously reported² 950°C data. The kinetics are approximately parabolic for these three exposure temperatures although there are distinct discontinuities in the curves. In Fig. 2, some of the data from

Fig. 1 are compared with the weight changes measured at 1100°C. The oxidation rate at this temperature showed breakaway behavior (see below) after about 100 h.

Fig. 1. Weight change versus time for binary Cr-12% Nb oxidized in air, 900 - 1000°C.

Fig. 2. Weight change versus time for binary Cr-12% Nb oxidized in air, 950 - 1100°C.

Figure 3 shows the effects of compositional modifications to Cr-12%Nb, as listed in Table 1, on isothermal oxidation kinetics in air at 950-965°C. Neither the addition of Al or Re, nor the reduction in interstitial levels (compare CN4A to CN46) proved to be beneficial. Indeed, the binary alloy showed better isothermal oxidation behavior than any of the more highly alloyed compositions. Approximate parabolic rate constants (fitted to the data for times greater than 40 h) ranged from $5\text{--}16 \times 10^{-5} \text{ mg}^2/\text{cm}^4\cdot\text{s}$ for these alloys compared to $2 \times 10^{-5} \text{ mg}^2/\text{cm}^4\cdot\text{s}$ for the binary composition. Visual examination of specimen surfaces after cooling from the exposure showed that, with the exception of CN4 and CN48, the more highly alloyed 12% Nb compositions suffered significant scale spallation. For the Cr-6% Nb alloy, the presence of 8% Al did not improve isothermal oxidation resistance; upon cooling from the exposure temperature, the spallation losses for CN7 and CN7A were comparable and the latter alloy showed higher weight gains and nonparabolic reaction kinetics.

Only the CN4, 4A, 7, and 7A alloys were exposed under cyclic oxidation conditions. The results for Cr-12% Nb are shown in Fig. 4, which also includes the 950°C isothermal data. Note that thermal cycling increased weight gains and spallation losses. The addition of 8% Al to Cr-12% Nb did not significantly change the cyclic oxidation behavior shown in Fig. 4. For both alloys, little spallation to bare metal was observed. As shown in Fig. 5, detachment was normally in the scale, albeit close to the interface with the alloy. A multiproduct scale formed and cracking was observed in more than one layer.

Fig. 3. Weight change versus time for Cr-12% Nb oxidized in air at 950 - 965°C.

Fig. 4. Weight change versus time for binary Cr-12% Nb oxidized in air at 950°C.

Fig. 5. Polished cross section of Cr-12% Nb-8% Al (CN4A) thermally cycled in air at 950°C for 268 h.

Figure 6 compares the weight changes for two binary Cr-6% Nb (CN7) specimens under thermal cycling conditions with results for the 950°C isothermal exposure. Scale spallation was visually observed after just a few cycles. As shown in Fig. 7, cyclic exposures of Cr-6%Nb-8%Al (CN7A) led to substantial mass gains at longer times. The Al-containing alloy showed less spallation than the binary composition. A fairly thick scale remained adherent to most of the CN7A specimen (Fig. 8), but some scale damage did occur (Fig. 9).

Fig. 6. Weight change versus time for Cr-6% Nb (CN7) oxidized in air at 950°C.

Fig. 7. Weight change versus time for Cr-6% Nb - 8% Al (CN7A) oxidized in air at 950°C.

Fig. 8. Polished cross section of scale formed on Cr-6% Nb-8% Al after cyclic oxidation at 950°C for 268 h.

Fig.9. Scanning electron micrograph of scale formed on Cr-6% Nb-8% Al after cyclic oxidation at 950°C for 268 h.

DISCUSSION

The thermogravimetric data at 900 and 1000°C (Fig. 1) are consistent with previously reported data at 900 and 950°C (ref. 3) in terms of the relative rates of weight gain and the generally parabolic shapes of the weight gain curves. The parabolic rate constants are within the relatively wide band of those reported for the oxidation of chromium.⁴

Results from a previous study of the oxidation of Cr-6 and -12% Nb alloys³ suggested that scale cracking occurs during isothermal exposure at 900 and 950°C. This conclusion was based on observation of intervals of parabolic kinetic behavior interrupted by abrupt increases in weight and was reinforced by similar results for the oxidation of chromium.⁵ Such behavior is normally ascribed to fracture of the oxide scale^{4,5}; after a critical scale thickness is reached, cracking occurs to relieve accumulated stresses caused by the growth of the reaction product. This can expose more reactive underlying material, thus leading to the rapid kinetics associated with the initial stages of oxidation. (In essence, the parabolic growth curve is reset to near zero time.) The process of cracking and healing can then repeat, leading to a sequence of parabolic (protective) stages.^{4,5} Some discontinuities in the thermogravimetric curves can also be observed in the data shown in Fig. 1. Given this tendency for scale cracking in the Cr-Nb system, it appears that the weight gain behavior observed for Cr-12% Nb at 1100°C (Fig. 2) can be explained in terms of a breakaway

oxidation phenomenon in which rapid scale growth produces cracking events at a frequency sufficiently high that the protective stages are very short and, therefore, approximately linear rate kinetics are observed.⁴ The shape of the thermogravimetric curve at 1100°C typifies classic breakaway oxidation behavior.⁴ The large weight gains and their linear dependence on time indicate that exposure of this alloy must be limited to air temperatures less than 1100°C.

Given the tendency for isothermal scale cracking, it is not surprising that significant spallation was observed during cyclic oxidation of many of the Cr-Nb alloys. Fig. 4 clearly shows higher weight gains of Cr-12% Nb under cyclic conditions, thereby indicating scale damage during each thermal cycle. In contrast to isothermal exposure, where little scale loss was noted at the end of an experiment,³ substantial spallation from Cr-12% Nb was observed after several cycles, and the presence of aluminum did not seem to improve scale adherence. Interestingly, there does appear to be some evidence that aluminum may improve the cyclic oxidation resistance of the binary Cr-6% Nb alloy, which showed substantial scale spallation under isothermal conditions³ and weight losses during thermal cycling (Fig. 6). As shown in Fig. 8, a complex, but relatively adherent scale on CN7A was observed in cross section, but, pending detailed compositional analysis, the mechanism by which aluminum may improve adherence remains unknown. However, it does not appear to be related to any effect of aluminum on phase distribution in Cr-Cr₂Nb (which can affect oxide growth and adherence³) as no significant differences in the microstructures of Cr-6% Nb and Cr-6% Nb-8% Al were found.

While aluminum may have improved the spallation resistance of Cr-6% Nb, it had a detrimental effect on isothermal kinetics (see above). Furthermore, it did not have any beneficial influence on Cr-12% Nb under either isothermal or cyclic oxidation conditions. Indeed, as shown in Fig. 3, neither aluminum or rhenium, nor reduction in impurity levels (which can deleteriously influence oxide growth on chromium^{6,7}) appear to improve the oxidation resistance of Cr-12% Nb. However, in view of what is known about chromia scales (see, for example, refs. 4, 6, and 8), the similarities between the oxidation of Cr-Nb and that of chromium (in terms of rate constants, Cr₂O₃ formation, and isothermal scale cracking)³ suggest that the most effective elements in affecting the growth and adherence of the oxides on Cr-Nb alloys may well be several that have yet to be examined (such as certain reactive/rare earth elements). It is pertinent to speculate that, in view of the scale cracking tendencies discussed above, any alloying additions that act to improve scale plasticity or modify growth stresses^{9,10} would be particularly effective in the Cr-Nb system.

2 of 3

SUMMARY AND CONCLUSIONS

An isothermal exposure temperature of 1100°C led to accelerated reaction of binary Cr-12% Nb manifested in the form of breakaway oxidation. Parabolic kinetics were observed at 900-1000°C, but there was evidence of isothermal scale cracking. The high weight gains and their linear dependence on time at 1100°C indicate that Cr-12% Nb must be limited to lower temperatures if exposed to air.

Scale damage was exacerbated by thermal cycling. The addition of 8% Al to Cr-12% Nb did not improve cyclic oxidation resistance, but there was some evidence that scale adherence on Cr-6%Nb-8% Al was better than on binary Cr-6% Nb.

Alloying additions of Al (up to 18%) or Re (2%) did not improve the isothermal oxidation resistance of Cr-12% Nb, nor did the reduction in the level of impurities. However, other alloying elements that lead to decreased growth rates and better scale adherence for chromia on chromium and Cr-containing alloys may provide opportunities for improved oxidation resistance of Cr-Cr₂Nb alloys. In particular, the tendency for scale damage during both isothermal and thermal cycling exposures suggests that alloying additions that specifically improve scale plasticity or modify growth stresses should be effective for Cr-Nb alloys.

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2.10 MATERIALS SUPPORT FOR HITAF

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INTRODUCTION

The purpose of this project is to compare structural ceramic materials proposed for use in the air heater of a coal fired high temperature advanced furnace (HITAF) for power generation. The work will provide necessary initial structural ceramics parameters for design of a prototype system. Two teams are currently funded by Pittsburgh Energy Technology Center (PETC) under the Combustion 2000 program to develop such a system. One team is lead by the United Technologies Research Corporation, and consists of UTC Turbo Power and Marine Division, Bechtel, Oak Ridge National Laboratory (ORNL), and a Joint Venture of Physical Sciences Inc. (PSI) Technologies, Reaction Engineering International (REI) and University of North Dakota Engineering and Environmental Research Center (UNDEERC). The other team is lead by Foster Wheeler Development Corporation, and members are AiResearch Division of Allied Signal Aerospace Company, Reserach Cottrell, TRW, and Bechtel.^{1,2}

DISCUSSION OF CURRENT ACTIVITIES

The present reporting period is the second period for this project. Both teams have developed the design concept of the overall system from the original proposals and the temperature and environments that the air heater materials will see as better defined.

The following key properties are being evaluated in the present task; fast fracture strength at room temperature, 1100°C and 1400°C; statistical analysis in the form of a Weibull analysis and necessary fractography; slow crack growth properties evaluated by the dynamic fatigue method; and creep/creep-rupture effects measured through interrupted static fatigue experiments. In addition, the two Combustion 2000 teams are performing initial corrosion experiments, and ORNL will perform fast fracture measurements of corroded specimens.

Fast fracture

The fracture strength of ceramic materials is most commonly measured in four-point flexure.³ In this test a specimen of 4x3x50mm is subjected to bending in a fixture providing an inner span of 20mm and an outer span of 40mm. The specimen is loaded to fracture while load and deflection are monitored, and the flexure strength is calculated according to standard beam theory. Alternatively fracture strength may be measured in a tensile test in which a circular rod with a narrow gauge section is pulled in tension to fracture with the aid of a complicated gripping system. The tensile method is better suited for evaluating mechanical properties of ceramics, however due to the cost of both the gripping system and the tensile specimens themselves, tensile testing of structural ceramics is not widely performed. In uniaxial tension the bulk properties are directly measured, and creep deflection can be measured directly. The flexure method offers the possibility of testing a large number of samples at a reasonable price, and since the load train arrangement is much simpler, several specimens may be tested simultaneously.

Weibull analysis

Weibull analysis is the statistical tool most commonly used to analyze fracture data for structural ceramics.⁴ Due to the brittle nature of ceramic materials, the fracture strength of a set of specimens may vary as much as 100% from its average strength, necessitating a statistical analysis of the data. The Weibull analysis is a weakest link theory stating that a given volume of a ceramic material under uniform stress will fail from the most severe flaw. The probability of failure is given by:

$$P_f = 1 - \exp \left[- \int V \left(\frac{\sigma_f}{S_0} \right)^m \right] \quad (1)$$

Where P_f is the failure probability, V the specimen volume, σ_f the fracture strength, m the Weibull modulus and S_0 the Weibull scaling factor.

The Weibull modulus m is used as a design parameter for ceramics and describes the spread in the strength data. The Weibull scaling parameter S_0 is related to the average strength of the sample. It is desirable that a structural ceramic have a high m and a high

S_0 . The Weibull parameters are directly obtained from strength data by for instance the maximum likelihood method:⁵

$$\frac{\Sigma[\ln\sigma(\sigma)^m]}{\Sigma(\sigma^m)} - \frac{1}{m} = \frac{\Sigma(\ln\sigma)}{N} \quad (2)$$

$$S_0 = \left[\frac{\Sigma(\sigma^m)}{N} \right]^{1/m} \quad (3)$$

where

σ is the fracture strength

N is the number of specimens

and m and S_0 are the Weibull parameters as described above

Fractography

The Weibull theory assumes that all failures used to generate the Weibull parameters are similar in nature, i.e., stem from the same type of flaws. This may not always be the case, most notably there will be a difference in flaws stemming from the powder pressing and sintering process and flaws stemming from machining and handling of the components. The purpose of performing a careful fractography is to identify the different sources of failure origins, and take that information into account by appropriately censoring the Weibull distribution.

Static and Dynamic Fatigue

The term "fatigue" as used for structural ceramics is different from that commonly used for metals. For ceramics the term fatigue is used to describe the decrease in strength due to the combined action of *static* stress and degrading environment. The mechanism which causes this is known as Slow Crack Growth (SCG) and is the growth of small preexisting cracks or voids at stress levels less than those needed to cause catastrophic

failure. This happens because the individual atomic bond strength is decreased due to the specific environment. Eventually, a small crack has grown to a size large enough to cause catastrophic failure at the given stress level. In order to predict the lifetime for components in a given environment, the velocity at which cracks grow at a given stress must be known.⁶

A static fatigue experiment is performed by loading a specimen to a given stress in the given environment and recording the time to failure. This type of test can be extremely time consuming (> 1000 hours) and several specimens are needed at each condition in order to obtain the required statistics. A common way to accelerate the test is to perform a dynamic fatigue experiment in which the specimens are loaded to failure at several given stressing rates and the fracture strength is recorded as a function of applied stressing rate.⁷ If a material is susceptible to SCG, the fracture strength will decrease as a function of decreasing stressing rate, and by applying the following fracture mechanics framework on the measured data, the SCG parameters may be determined. The crack velocity during slow crack growth is often described in a power law form:

$$V = A \left(\frac{K_{\text{appl}}}{K_{\text{IC}}} \right)^n \quad (4)$$

where

K_{appl} is applied stress intensity,
 K_{IC} is the critical stress intensity,
 V is the crack growth velocity and
 A and n are materials constants.

Combining this with the Griffith criteria for fast fracture strength:

$$\sigma_i = Y K_{\text{IC}} c^{-1/2} \quad (5)$$

where

σ_i is the strength,
 c is the crack length and
 Y a specimen geometry and crack shape parameter.

The time to failure under constant applied stress may be obtained:

$$t_f = B \sigma_i^{n-2} \sigma_f^{-n} \quad (6)$$

where

$$B = \frac{2 K_{IC}^2}{(n-2)AY^2} \quad \text{is a material constant,}$$

and

t_f = Time to failure

σ_f = Fatigue strength

σ_i = Fast fracture strength (inert)

In the case of the dynamic fatigue experiment, the equations combine to give

$$t_f = B (n+1) \sigma_{inert}^{n-2} \sigma_f^{-n} \quad (7)$$

and

$$\sigma_{fatigue}^{n+1} = B (n+1) \sigma_i^{n-2} \dot{\sigma} \quad (8)$$

where

$\dot{\sigma}$ = Applied stressing rate

and the fatigue parameter n is obtained by plotting $\log \sigma_f$ vs $\log \dot{\sigma}$.

Interrupted static fatigue is a method to supplement the dynamic fatigue data. The specimens are held at a load known to be a certain percentage of the actual fast fracture load at the given environment, and after a given time the test is interrupted and the remaining strength is measured by loading the specimen to failure. In this manner a limited information about the tendency for a material to creep is also obtained.

EXPERIMENTAL RESULTS

To date, two materials have been selected by the UTRC team. NT230 which is a siliconized silicon carbide (SiC) produced by Saint-Gobain/Norton Company and Lanxide Dimox, a silicon carbide particulate reinforced aluminum oxide produced by Lanxide. The manufacturers material data are presented in Table 1.

All specimens are four-point bend bars with dimensions 3x4x50mm with chamfered edges. All measurements are performed using a hydraulic flexure testing facility with silicon carbide bend fixtures with outer span of 40mm and an inner span of 20mm. Fast fracture is measured at Room Temperature using a stressing rate of 37MPa/s and dynamic fatigue experiments are carried out at 1100°C and 1400°C using stressing rates of 1, 0.01, 0.001 and 0.0001MPa/s, resulting in times to failure of typically 3 min, 11h, 110h and 1100h, respectively. Figures 1 and 2 show the fast fracture strength as a function of temperature for NT230 and Lanxide Dimox respectively. Figure 3 is a Weibull plot of the room temperature fracture strength of NT230. Note that this figure is meant as an illustration of the Weibull graph, as the 9 data points obtained to date are too few to give a statistically valid determination of the Weibull parameters.

Figures 4, 5, 6 and 7 are the dynamic fatigue results of the two materials at 1100°C and 1400°C. A summary of the strength results is given in Table 2.

DISCUSSION AND SUMMARY

The fast fracture as a function of temperature is different for the two materials. NT230 keeps its strength level of approximately 400MPa up to 1100°C after which it drops off. Lanxide Dimox loses strength at a much lower temperature, but does maintain some residual strength up to 1400°C.

The four dynamic fatigue graphs in Figures 4 through 7 show that none of the materials exhibit significant slow crack growth at the two temperatures in air. This is a very important result as several other ceramics will exhibit significant slow crack growth at these temperatures in air.⁸

However, not evidenced from the dynamic fatigue analysis are the creep tendencies, especially for Lanxide Dimox at 1400°C. The creep deformation at 1400°C for this material is large, and the dynamic fatigue experiments at the lowest stressing rates will not be carried out. At these times the creep will be excessive and it will no longer be meaningful to carry out a flexure test.

Microstructural observations show that there are significant amounts of free metal in both materials, Al and Si in the Lanxide and NT230 respectively. At 1400°C the free metal starts to leak out, and even at fairly short exposure times (<10h) beads of free metal exist on the specimen surfaces.

In summary, the tests carried out in air so far indicate that both NT230 and Lanxide Dimox have acceptable properties at 1100°C but that serious problems i.e. excessive creep of Lanxide Dimox and loss of strength for NT230, exist at temperatures around 1400°C.

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Table 1. Material Data

NT 230 Siliconized Silicon Carbide (SiC), Saint-Gobain Norton		
8 Vol% Si - metal		
90 Vol% SiC		
2 Vol% Pores		
Lanxide Dimox Aluminium Oxide with Silicon Carbide Particles, Lanxide		
40 Vol% SiC	Desity 3.4 g/cm ³	
38 Vol% Al	Thermal Conductivity 60Wm/K	
13 Vol% Al - metal	Thermal Expansion 7 /°C	
1 Vol% Pores	Fracture Toughness 7.0MPam ^{1/2}	

Table 2. Summary of results from the dynamic fatigue experiments.

Stressing Rate [MPa/s]	Mean Strength NT230 [MPa]			Mean Strength Lanxide [MPa]		
	RT	1100°C	1400°C	RT	1100°C	1400°C
37	372.1	427.2	176.2	404.8	228.2	206.2
1.0		412.8	228.9		233.8	208.2
0.01		343.3	160.0		283.9	219.9
0.001		475.2	160.6		242.9	
0.0001		445.4	176.9		218.6

Figure 1. Fast fracture as a function of temperature for NT230

Figure 2. Fast fracture as a function of temperature for Lanxide

Figure 3. Weibull plot of fast fracture strength for NT230 at Room Temperature.

Figure 4. Fracture stress as a function of stressing rate for NT230 at 1100°C.

Figure 5. Fracture stress as a function of stressing rate for NT230 at 1400°C.

Figure 6. Fracture stress as a function of stressing rate for Lanxide at 1100°C.

Figure 7. Fracture stress as a function of stressing rate for Lanxide at 1400°C.

3. ENVIRONMENTAL ANALYSIS SUPPORT

R.L. Miller

Activities in environmental analysis support included assistance to the Morgantown and Pittsburgh Energy Technology Centers (METC and PETC) in reviewing and preparing documents required by the National Environmental Policy Act (NEPA) for several projects selected for the Clean Coal Technology Program. A key activity was the preparation for PETC of a draft Environmental Impact Statement (EIS) for the Healy Clean Coal Project in Healy, Alaska. This work is notable because it is the first site-specific EIS prepared for the Clean Coal Technology Program. In addition, work began for METC on the preparation of a preliminary draft EIS for the Des Moines Energy Center Repowering Project in Pleasant Hill, Iowa. Another important activity was the preparation of a preliminary draft Programmatic Environmental Assessment (PEA) for DOE's Oil Research Program. Finally, ORNL is assisting DOE/FE in the preparation of an Action Description Memorandum for the continued funding of the fossil research and development program directed by METC.

3.1 ENVIRONMENTAL SUPPORT TO THE CLEAN COAL TECHNOLOGY PROGRAM

R.L. Miller

Work during this six-month period focused on the preparation for DOE's Pittsburgh Energy Technology Center (PETC) of a draft Environmental Impact Statement (EIS) for the Healy Clean Coal Project (HCCP). The project, proposed by the Alaska Industrial Development and Export Authority and selected by DOE in the third solicitation of the Clean Coal Technology Program, would be located in Healy, Alaska, about 4 miles north of the nearest border of Denali National Park and Preserve (DNPP). The proposed project is a new 50 megawatt coal-fired power generating facility that would be collocated with an existing 25 megawatt conventional pulverized-coal unit owned and operated by Golden Valley Electric Association. The new facility would feature integration of advanced combustion and flue gas cleanup technologies to reduce emissions of SO₂ and NO_x. The draft EIS, released to the public in November 1992, is notable because it is the first site-specific EIS prepared for the Clean Coal Technology Program. Public hearings on the draft EIS were held in Alaska in December 1992, and work has begun on revising the EIS to produce a final version.

Impacts to air quality, surface water, groundwater, and ecological and socioeconomic resources from construction and operation of the HCCP were evaluated and results indicate that, for most resource areas, the impacts are not expected to be major. Tentative findings for areas of potential concern are summarized below. Of primary concern, as predicted by analyses based on computer models, is the degradation of air quality and visibility expected in portions of DNPP because of HCCP operation. Also, during the winter, the length of ice-free water in the Nenana River downstream of the HCCP is expected to increase because of the HCCP's thermal discharge of once-through cooling water. Consequently, ice bridge formation on the river at the village of Ferry, located about 10 miles downstream, may be affected (the ice bridge is used by residents to transport supplies across the river during winter). Finally, socioeconomic impacts are expected during construction and operation of the HCCP, particularly in the areas of housing, education, traffic, police and fire protection, and medical services.

In addition to the above EIS, a preliminary draft EIS for the Des Moines Energy Center (DMEC) Pressurized Circulating Fluidized Bed (PCFB) Repowering Project was prepared for DOE's Morgantown Energy Technology Center (METC). This EIS is the second site-specific EIS prepared for the Clean Coal Technology Program and the first one prepared for METC. The DMEC project would power a new gas turbine and repower an existing steam turbine by replacing a boiler with a new PCFB combustor at the DMEC site in Pleasant Hill, Iowa, near Des Moines, Iowa. Proposed by Dairyland Power Cooperative and Midwest Power and selected by DOE in the third solicitation of the Clean Coal Technology Program, the project would generate approximately 80 megawatts of electricity. The project, the world's first large-scale demonstration of PCFB technology, is expected to produce valuable data to assess plant reliability and performance that could lead to widespread commercial application of PCFB technology.

The following findings resulted from the assessment of potential impacts to resource areas. During DMEC operation, maximum concentrations of SO_2 and NO_x at or beyond the DMEC perimeter are expected to be less than 15% of applicable standards. Maximum particulate concentrations are expected to be near the short-term standards, but almost all of the concentrations would result from fugitive dust from the DMEC coal pile rather than stack emissions. DMEC operation could affect the Des Moines River through withdrawal of shallow groundwater and discharge of wastewaters and runoff, but net consumption of river water would represent less than 0.07% of the average river flow. Under existing conditions of water demand and availability, the proposed rates of water withdrawal would have only minor and temporary effects on aquatic communities during low-flow conditions. Because there are no jurisdictional (designated) wetlands within the DMEC site, no wetland impacts would occur as a result of facility operation. Although the red canary grass community (which would be lost upon construction and use of the ash disposal area) is a wetland type of vegetation and has wetland functions, the DMEC site is not considered a jurisdictional wetland because it lacks hydric soil properties. The proposed ash disposal area should accommodate the volume of ash generated for the lifetime of the project. Construction and operations at the DMEC site are expected to disturb bald eagles roosting nearby; as a result, the eagles may discontinue using the area adjacent to the site as a winter roosting area. However, any impacts are not expected to have a serious effect on the eagles because they use the area intermittently rather than daily. Renovation of the DMEC facilities is expected

to improve the visual appearance of the DMEC site, although the architectural integrity of the powerhouse, eligible for historic preservation on the National Register of Historic Places, would be altered during construction of the proposed project. Mitigation measures are available to minimize impacts to cultural and aesthetic qualities associated with the structure. The project would result in the loss of quiet along the Des Moines River near the DMEC site, but other quiet areas along the river probably would compensate.

3.2 ENVIRONMENTAL SUPPORT TO METC R&D PROJECTS

R.L. Kroodsmma

During this six-month period, a preliminary draft Environmental Assessment (EA) for the proposed Gasification Product Improvement Facility (GPIF) at the Fort Martin Power Station (FMPS) was prepared for DOE's Morgantown Energy Technology Center (METC). The GPIF would use coal to produce a fuel gas that would be combusted to provide steam for electrical generation in one of the two units at the existing coal-fired FMPS located north of Morgantown, West Virginia. The proposed project would develop, demonstrate, and enhance commercialization of an advanced technology for gasification of coal.

The GPIF would include two subsystems that would be constructed in two consecutive phases. Phase I includes the construction and demonstration of a gasifier and the burning of the fuel gas to produce steam for electrical generation by the FMPS. In Phase II, a facility for cleaning the fuel gas from the gasifier would be constructed and demonstrated during continued gasifier operation. High sulfur coal would be burned during Phase II to thoroughly test the gasifier's and hot gas cleanup system's ability to limit sulfur emissions.

Environmental impacts to resource areas resulting from construction and operation of the GPIF were evaluated and preliminary results indicate that the impacts are not expected to be major. The GPIF is expected to produce a clean fuel gas while minimizing the emissions of air pollutants. Surface water but no groundwater at the FMPS site would be withdrawn for the GPIF. GPIF consumption of Monongahela River water would represent about 0.34% of the river's low flow and 0.02% of average flow. Groundwater and surface waters receiving drainage from the FMPS ash disposal pile, where GPIF ash would be disposed, should not be impacted by the GPIF, because the leachability of contaminants in the GPIF is expected to be less than that in FMPS ash. No wetland or 500-year floodplain is present on the GPIF site. The GPIF would have no substantial impact on aquatic or terrestrial biota. The proposed GPIF site is already a disturbed area adjacent to the existing FMPS and does not provide important habitat for plants or animals. Socioeconomics would not be appreciably affected, because of the small size of the proposed project and its small

expected employment of only about 20 to 25 people during construction and operation. Because of the existing disturbance at the proposed GPIF site, no significant cultural resources are expected to be present.

3.3 OIL RESEARCH PROGRAM ENVIRONMENTAL SUPPORT

R.L. Miller

No substantial progress during the reporting period.

3.4 ACTION DESCRIPTION MEMORANDUM FOR METC R&D PROGRAM

J.T. Ensminger

During the reporting period, ORNL prepared review drafts for DOE/FE of an Action Description Memorandum (ADM) for the continued funding of the fossil R&D program that is currently directed by METC. The METC R&D program consists of 309 individual projects that fall into eight programs areas. The ADM addresses the potential impacts of the overall R&D program rather than impacts of individual projects since the latter are addressed individually under DOE's NEPA Implementation Procedures (10 CFR 1021). In general, the individual projects are relatively small (median funding level of \$1 million), short-term (median duration of about three years), and widely dispersed geographically. The vast majority of projects are conducted in existing facilities and produce only minor changes in the environmental impacts of those facilities. Potential programmatic issues identified in the ADM include: (1) cumulative impacts resulting from multiple projects occurring in the same time frame and at the same or nearby locations; (2) impacts from eventual commercialization of concepts developed under the R&D program; (3) stimulated interest in the use of fossil relative to non-fossil technologies; and (4) concerns regarding NEPA compliance. The determination of the ADM is that no programmatic NEPA documents are warranted for the eight METC R&D program areas. Determinations have been made for 264 of the 309 projects included in the METC program: 242 are covered by Categorical Exclusions or Memos-to-file; 22 require Environmental Assessments; and none require an Environmental Impact Statement. The ADM will be used as the basis for DOE's decision on the appropriate level of NEPA documentation (Categorical Exclusion, Environmental Assessment or Environmental Impact Statement) for the remaining projects in the R&D program.

3.5 SUPPORT TO THE WILSONVILLE COAL LIQUEFACTION R&D FACILITY

F.G. Gardner, P.M. Kearl, and N.E. Korte

INTRODUCTION

The purpose of this task is to support the Pittsburgh Energy Technology Center (PETC) and their prime contractor Southern Company Services, Inc. in satisfying National Environmental Policy Act (NEPA) requirements for the retirement and dismantling of the Advanced Coal Liquefaction Research and Development (ACLR&D) Facility in Wilsonville, Alabama. Oak Ridge National Laboratory (ORNL) is assisting PETC in obtaining a sufficient waste characterization and hydrogeologic assessment to satisfy the current requirements of NEPA.

The primary field tasks involve the establishment of a hydrogeologic monitoring system and a characterization of potential waste areas. Information from these activities will be incorporated into an Environmental Assessment (EA) that will describe the potential impacts resulting from the decommissioning of the site.

DISCUSSION OF CURRENT ACTIVITIES

The initial activities conducted during fiscal 1993 were the completion of an extensive seismic survey that was needed to further delineate the subsurface geology. Following the seismic fieldwork, extensive data reduction was required which has now been completed and has been used to plan additional drilling.

The hydrogeology at the site is quite complex consisting of relatively impermeable surface material underlain in some locations by karst. Because there apparently has been numerous episodes of folding and faulting, more work is necessary to adequately describe the site hydrogeology. Moreover, the full extent of soil and groundwater contamination has not been delineated both because more wells are needed to assess the downgradient extent of contaminated groundwater and because of access limitations due to the presence of the equipment remaining on site. These data gaps are expected to be satisfied by a series of field activities that will be initiated in April 1993. Additional downgradient monitoring wells and additional soil sampling in waste areas are planned. Characterization of the hydrogeologic system will continue with the installation of additional coreholes.

Data from the coreholes are needed to determine the extent of the connection between the highly contaminated shallow groundwater and the limestone aquifer underlying the site. It should be noted that the contamination in the surface unit, of itself, is only a minor threat to the environment because the unit is not very permeable. Indeed, the water level does not recover in several of the wells for hours or days following purging. On the other hand, potential contamination in the limestone aquifer would be a serious concern because it is a productive formation. Fortunately, while there are water supply wells utilizing the deeper aquifers in this area, none of the supply wells are near the Wilsonville site. Hence, there is no immediate possibility of human or environmental exposure.

The additional fieldwork that is required is expected to be completed during June of 1993. A draft report describing the hydrogeology and its implications regarding environmental risk and potential remedial scenarios will be provided to PETC by the end of fiscal year 1993.

4. COAL CONVERSION DEVELOPMENT

C. D. Scott

Fundamental bioprocessing research has concentrated on the use of biocatalysts in organic media and on advanced bioreactor systems. Coal conversion research has continued on the biological solubilization of coal using chemically-modified enzymes in organic solvents. Biophotolysis is being studied for the production of hydrogen. Activities are also continuing on the study of mild gasification of coal.

4.1 BIOLOGICAL CATALYST IN ORGANIC MEDIA

C. D. Scott

Several potential coal bioprocessing concepts may utilize an organic solvent and/or produce liquid organic products. In either case, it will be necessary for the biological catalyst to be active in contact with or within the organic media. The major technical challenge associated with the use of biocatalysts in organic solvents is the maintenance of catalyst integrity and, in the case of intact cells, the viability of the microbial structure. Microorganisms or active biological fractions (e.g., enzymes) cannot normally maintain activity in an organic media; however, it may be possible to use microorganisms in a controlled aqueous environment that can be dispersed into the organic. Extracted enzymes may even be chemically modified so that they will dissolve in the organic media while maintaining catalytic activity.

ORNL RESEARCH ON ENZYME SOLUBILIZATION IN ORGANIC MEDIA

The primary effort in this task continues to be the chemical modification of enzymes to increase hydrophobicity and, thus, solubilization in organic solvents while maintaining catalytic activity. Such modified biocatalysts could have a variety of uses for enhancing chemical interactions in organic liquids, especially when a hydrophobic solid substrate such as coal is the feed material. Dinitrofluorobenzene (DNFB) continues to be one of the most useful reagents for such a modification; however, other reagents including phenylacetaldehyde, fatty acid anhydrides, and two activated polyethylene glycols (PEGs) are also being evaluated. The major emphasis this quarter has been on establishing the optimum conditions for enzyme modification with the activated PEGs so that they can be compared with the results from the other approaches previously studied.

Organic Liquids

Organic liquids used in this study include pyridine and p-cresol, relatively polar compounds, benzene, a relatively nonpolar solvent, and an organic mixture (45% tetralin, 40% 2-methylnaphthalene, and 15% p-cresol) that should have properties somewhat similar to the light fraction from coal derived liquids. Use of these organic liquids allows an evaluation of effects over a wide range of hydrophobicity. All of these organic compounds were used as reagent grade chemicals.

Model Enzymes

Two proteins/enzymes continue to be used as the model proteinaceous material for testing chemical modification to enhance solubilization in organic liquids. These are a crude hydrogenase preparation from *Proteus vulgaris* (isolation techniques have been previously described) and cytochrome c obtained from Sigma Chemical Co.

Enzyme Modification with Activated PEG

Two types of activated PEGs that were specifically developed for interaction with proteins are now available from Sigma Chemical Co. These are methoxypolyethylene glycols activated with cyanuric chloride (PEG-c) and that activated with p-nitrophenyl carbonate (PEG-n). Both of these reagents were originally developed as reagents for research with proteins, primarily with the aim of enhancing stability in aqueous solutions;^{2,3} however, with some modification in the reaction sequence we are now studying the use of such reagents for increasing the hydrophobicity of enzymes. Our Laboratory had done some work with PEG-c before but a more systematic investigation is now being carried out. As with most of the other chemical reagents that we have studied, these compounds tend to react with the free amine groups found on the protein molecules.

The conditions developed for these chemical modifications was to introduce the protein at a concentration of 5-10 mg/mL into an agitated, buffered aqueous mixture (.2M borate buffer at a pH of 10 for PEG-c and 8.8 for PEG-n) containing 30-100 mg/mL of the

activated PEG. The reaction proceeded for 1 h with PEG-c and 2 h with PEG-n after which the pH was adjusted to 7.8 to terminate the reaction by addition of 1 N HCl. This mixture was then dialyzed overnight against 7mM phosphate buffer at a pH of 7.8. Then the solution was lyophilized and the resulting solid material was used or stored at 0°C.

The solubility of the resulting modified enzyme was studied by contacting the lyophilized material with nonhydrous organic solvents for 1 h after which the remaining solids were removed by centrifugation for 10 min at approximately 1000 G. Hydrogenase activity was determined by a previously described technique.^{1,4} The activity was measured directly in the aqueous phases and indirectly in the organic phase by removing the organic by drying and then resolubilizing in an aqueous buffer.

Solubility of the modified enzyme was affected by both the chemical reagent used and the organic solvent used. Modification with PEG-n resulted in as much as a three-fold increase in solubility when compared with the enzymes modified with PEG-c. There was also a significant increase in solubility when the more polar solvents (pyridine and p-cresol) were used when compared to the less polar benzene. For example, almost all of the enzyme modified with PEG-n was dissolved in p-cresol. The chemical modification with PEG-n has resulted in the best results for solubilization in organic solvents as any modification reagent tested to date.

Enzyme activity is also an important criteria for choice of the modification reagent. There is usually a decrease in activity with each step of the modification procedure (chemical interaction, dialysis, lyophilization, and contact with the organic). For example, during the chemical interaction step 45-61% of the activity was lost when PEG-c was used but generally over 90% of the activity was maintained when PEG-n was used. An additional 20% of the enzyme activity was usually lost during dialysis and there was an additional loss during lyophilization. It was again, observed that PEG-n was superior in maintaining enzyme activity in the organic solvent with almost an order-of-magnitude difference when compared to the use of PEG-c (Table 1). As observed in the past, the specific activity of modified enzymes dissolved in the less polar solvents (benzene, etc.) is always higher than for the more polar solvents (pyridine, etc.). Even though the amount of modified enzyme is greater in pyridine

than benzene, the actual catalytic activity is much greater in the benzene and to a lesser degree to p-cresol with this type of enzyme modification.

Table 1. Catalytic Activity of Hydrogenase that Remained after Chemical Modification and Solution in Organic Solvents

Solvent	Enzyme Activity (Units/mL)
<u>Modified with PEG-c</u>	
Benzene	.03
Pyridine	<.01
<u>Modified with PEG-n</u>	
Benzene	2.29
p-Cresol	.63
Pyridine	.14

The PEG-n reagent is obviously superior in several ways over some of the other reagents that have been evaluated. Additional studies on this type of enzyme modification will be carried out in the future.

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MICROBIAL REMOVAL OF COAL HETEROATOMS

This work examines the potential utility of anaerobic microorganisms in the removal of sulfur, nitrogen, and other heteroatoms from coal-derived liquids. The desired activity would result in the formation of intact and/or reduced hydrocarbon products. Sulfur removal has formed an initial focus of this effort.

Previous efforts at ORNL and elsewhere have resulted in the identification of several types of organisms (including heterotrophic bacteria and fungi) capable of desulfurizing aromatic coal substructure model compounds such as dibenzothiophene (DBT). These organisms were aerobic. Organic sulfur removal was achieved via oxidation of the sulfur atom, which was released as sulfate. However, this desulfurization activity also resulted in the introduction of oxygen into the organic product. In some cases an undesirable oxidative cleavage of the homoatomic ring was also observed.

The current work has attempted to circumvent these problems via the use of anaerobic systems favoring a sulfur-specific attack. Judicious choice of catalyst would facilitate a substrate-level oxidation of the sulfur atom and its subsequent removal, in the absence of ring oxygenation. Developmental efforts have focused on the application of anaerobic phototrophic bacteria in the removal of sulfur from coal-derived substrates, with an initial emphasis on desulfurization of DBT.

Organisms capable of anoxygenic photosynthesis fall into two broad categories, namely the sulfur and nonsulfur bacteria. Each category can be divided further into two groups on a basis of cell color, which is conferred by photosynthetic pigments. The purple sulfur bacteria, the green sulfur bacteria, and the purple nonsulfur bacteria are well known. The green nonsulfur bacteria were isolated only very recently and have not been well characterized. The sulfur bacteria are strictly anaerobic, whereas the nonsulfur bacteria can usually survive exposure to oxygen.

Anoxygenic bacterial photosynthesis may be described as follows:

Suitable electron donors include S^{2-} , S^0 , $S_2O_3^{2-}$, H_2 , and partially reduced organic compounds. Photosynthetic activity typically supports the fixation of CO_2 as a source of cellular carbon. However, partially-reduced organic compounds can sometimes substitute for CO_2 .

Organic sulfur exists in the -2 state, which is analogous to S^{2-} . Organisms able to oxidize S^{2-} to S^0 and/or SO_4^{2-} may be able to oxidize organic sulfur. A specific, oxidative attack on the heteroatom would result in its cleavage from the organic compound, yielding soluble SO_4^{2-} . This activity would be analogous to that observed in aerobic systems. However, under anaerobic and/or reducing conditions within cultures of the sulfur bacteria, the organic residue would be unlikely to become highly oxidized or degraded. Sulfur-based photosynthesis in the presence of CO_2 may support the selective removal of sulfur from heteroatomic organic substrates, with no effect on the organic residue. Sulfur-based photosynthesis in the absence of CO_2 may support removal of sulfur from heteroatomic organic substrates coupled with incomplete degradation of the organic moiety to yield reduced products.

There is considerable variation among the anaerobic phototrophs with regard to sulfur and carbon metabolism. The green and purple sulfur bacteria are primarily photoautotrophic. The green sulfur bacteria grow at the expense of either S^{2-} (preferred), S^0 , or $S_2O_3^{2-}$, plus CO_2 . Organic carbon is not utilized as an electron donor and is not consumed as a carbon source unless CO_2 is also present. The purple sulfur bacteria use S^{2-} (preferred) or S^0 as a source of electrons, plus CO_2 (preferred) or organic compounds. These latter organisms can also use organic compounds as both electron donor and carbon source. Both types of sulfur bacteria convert S^{2-} to SO_4^{2-} via S^0 as an intermediate storage product. Most strains obtain cellular sulfur from S^{2-} only, i.e., cannot use exogenously-supplied SO_4^{2-} . In contrast, the nonsulfur bacteria are primarily heterotrophic, and indeed are capable of chemotrophic growth in the absence of light. The purple and presumably the green nonsulfur bacteria utilize organic carbon (preferred) or reduced sulfur as electron donor, and organic carbon (preferred) or CO_2 as carbon source. Under reducing conditions, the purple nonsulfur bacteria can carry out a unique reductive assimilation of organic compounds, in some cases converting aromatic compounds to saturated aromatic or aliphatic acids. Most strains of nonsulfur bacteria obtain cell sulfur from exogenously-supplied SO_4^{2-} .

The metabolic diversity of the anaerobic phototrophs suggests a similar variability in the fate of organic sulfur compounds such as DBT. The sulfur bacteria would be expected to be the superior catalysts for desulfurization of organic substrates. Both the green and the purple sulfur bacteria may carry out an oxidative attack on the sulfur atom of DBT, resulting in its removal. Sulfur extracted by these organisms may be incorporated into biomass, or may accumulate as the elemental form. Sulfur removal by green sulfur bacteria would be expected to occur without further action on the ring systems. However, sulfur removal by the purple sulfur bacteria may occur in conjunction with oxidation of the ring system, possibly followed by cleavage to form low-molecular-weight reduced products. The fate of DBT in cultures of nonsulfur bacteria cannot be readily predicted. The purple or green nonsulfur bacteria may form oxidized or reduced organic products from DBT, with or without selective removal of organic sulfur.

Work during this period comprised a preliminary screening of the ability of the anaerobic phototrophs to grow at the expense of DBT, i.e., to utilize DBT as a source of sulfur, carbon, and/or reducing equivalents. This work will test the feasibility of processes based on these organisms for the selective removal of sulfur from coal or coal-derived materials.

Isolation of Test Cultures

Experimental cultures were obtained by sampling of anaerobic environments in the vicinity of Oak Ridge. Samples of soils and sediments were inoculated into standard media for enrichment of green sulfur bacteria, purple sulfur bacteria, or purple nonsulfur bacteria.¹ Enrichment media for green sulfur bacteria were wholly inorganic and contained S^{2-} (Medium 1) or S^{2-} and $S_2O_3^{2-}$ (Medium 2). Enrichment medium (Medium 3) for purple sulfur bacteria contained a small amount of malate, a readily-metabolizable reduced carbon source. Media for the green and purple sulfur bacteria also contained SO_4^{2-} . Enrichment medium (Medium 4) for purple nonsulfur bacteria contained malate, ethanol, and yeast extract. Cultures were grown in these media for three passages of 14 d each. Eighteen stock cultures were obtained by these enrichments. All cultures appeared to be heterogenous. In particular, the purple

nonsulfur cultures appeared to contain high proportions of colorless nonphotosynthesizers. Stock cultures were maintained on the appropriate enrichment medium.

Microbial Metabolism of DBT

The following tests were performed using parallel cultures of green sulfur bacteria, purple sulfur bacteria, and purple nonsulfur bacteria. Stock cultures (50-mL vol) were harvested by centrifugation and washed three times with distilled water. The cell pellet was resuspended in 10 ml of water and a 1 mL sample was reinoculated into 50 mL of each of two experimental media. One experimental medium consisted of Medium 1-4 amended to contain 2 mM DBT, supplied as a solution in dimethylformamide (DMF). The final concentration of DMF in cultures was 5% (v/v). This medium formulation would allow cometabolism of DBT as an auxiliary source of sulfur, carbon, and/or reducing equivalents. This formulation also provided a preliminary screening for toxicity of DBT. As only cultures capable of growing in the presence of DBT were to be carried forward in planned experiments, parallel cultures grown in Medium 1-4 lacking DBT were omitted from this initial screening (although stock cultures in these media were conserved). The second experimental medium consisted of Medium 1-4 modified to contain 2 mM DBT in 5% DMF (final concentration) as sole source of reduced sulfur, reduced carbon, or both. All cultures were incubated under an atmosphere of 90% N₂:5% H₂:5%CO₂. Growth was monitored visually over 12 d. Cultures were extracted twice with an equal volume of methylene chloride, and metabolic products in the extract were analyzed by thin layer chromatography.

Surprisingly, each of the eighteen cultures obtained by sampling and enrichment were capable of growing in the presence of DBT (Table 2). All thirteen cultures of sulfur bacteria grew in media containing DBT as sole source of reduced sulfur. Most of these cultures grew nearly as well within medium containing DBT as sole reduced sulfur source as they did within media containing reduced inorganic sulfur plus DBT. The obligatory requirement of most sulfur bacteria for S²⁻ as a source of cell sulfur suggests that sulfur atoms were made available from DBT as a consequence of cellular activity. The ability of the obligately autotrophic

Table 2. Effect of DBT on growth of anaerobic phototrophic bacteria ($N_2:CO_2:H_2$ atmosphere).^a

Culture	Nutritional regime (DBT function)			
	Cometabolic substrate	Sole source of reduced sulfur	Sole source of organic carbon	Sole source of reduced sulfur and organic carbon
Green sulfur bacteria				
A1	+++	++		
B1	+++++	+++++		
C1	+	++		
D1	+++	++		
E1	+++++	+++++		
A2	+++	+++		
D2	++	++		
E2	++	+		
Purple sulfur bacteria				
A3	+++	++	+	++
B3	+++++	+++	+	+
C3	++	+	0 ⁺	0
D3	+++++	+++	+	++
E3	+++	++	0	+
Purple non-sulfur bacteria				
A4	++		+	
B4	+++		+++++	
C4	++		+++++	
D4	++		+++	
E4	+++		+++++	

^a Growth estimated by visual inspection on day 6: 0, none; +, poor; ++, average; +++, good; +++, excellent. Shaded area: not tested.

green sulfur bacteria to utilize DBT as an organic carbon source was not tested. However, three of five purple sulfur bacterial cultures produced a small amount of biomass within media containing DBT as sole source of reduced carbon. This finding suggested that DBT is at best poorly utilized by these cultures, and that growth under these conditions was primarily autotrophic. Four of the five cultures of purple sulfur bacteria tested grew in medium containing DBT as sole source of reduced sulfur plus reduced carbon. Intriguingly, in all but one of these cases slightly better growth occurred in medium where DBT was sole source of reduced carbon and sulfur than where DBT was sole source of reduced carbon only. This finding suggests an enrichment for DBT-degrading activity in sulfur-limited cultures. All sulfur bacteria tested here grew only in the presence of light (**data not shown**), confirming their phototrophic mode of existence. The purple nonsulfur bacteria, however, grew in the dark even in a solution containing 2 mM DBT in 5% DMF, i.e., in the absence of other nutrients (**data not shown**). DBT was also apparently well utilized by the latter organisms as a source of carbon, in the presence of yeast extract. The significant reduction of pH in these cultures (**data not shown**) suggests that DBT was extensively degraded, to acids. The ability of purple nonsulfur bacteria to utilize DBT as sole sulfur source was not tested.

Chromatographic analysis of the test cultures indicated the formation of products with greater polarity than that of DBT (Table 3). These products were nonfluorescent and were not susceptible to oxidative browning. These products thus appeared to be distinct from DBT sulfone and 1,1'-dihydroxybiphenyl, products known to be generated during a sulfur-specific aerobic attack. A separate, potentially phenolic product that migrated with DBT but which was susceptible to oxidative browning was also detected. Analysis of these products is underway.

This preliminary screening suggested that DBT is susceptible to microbial attack. Interpretation of the results of the preceding experiments is confounded by the presence in the headspace of H_2 , which can be utilized by all anaerobic phototrophs as a source of electrons. The presence of high concentrations of CO_2 , a preferred carbon source, also may have masked heterotrophic degradation of DBT. Subsequent work focused on confirming the oxidative activity of the anaerobic phototrophic bacteria toward DBT and its susceptibility to extensive degradation.

Table 3. Thin-layer chromatographic analysis of extracts of anaerobic phototrophic cultures containing DBT: Representative results (purple sulfur bacteria; N₂:CO₂:H₂ atmosphere).^a

Sample/culture	Condition	R _f values ^b						
Standards								
Blank	N/A				.53			
DBT	N/A				.52			1
DBT sulfone	N/A				.54		.62	
Biphenol	N/A				.51		.62	
Biphenyl	N/A				.50			1
Purple sulfur bacteria								
A3	cometabolism				.53			1.0
	sole S				.53		.59	1.0
	sole C			.46	.52			1.0
	sole S+C			.47			.59	1.0
B3	cometabolism				.50	.56		1.0
	sole S				.50			1.0
	sole C			.46	.52			1.0
	sole S+C			.46	.56			1.0
C3	cometabolism			.45	.52			1.0
	sole S				.52	.58		.95
	sole C			.49				1.0
	sole S+C				.51			1.0
D3	cometabolism			.49	.52		.59	1.0
	sole S	.33	.44	.48	.55			.96
	sole C				.51			1.0
	sole S+C			.48	.52			1.0
E3	cometabolism				.53			1.0
	sole S				.54			1.0
	sole C					.57		1.0
	sole S+C				.55			.99

^a Immobile phase: silica. Mobile phase: acetone:heptane (1:1).

^b R_f values were tabulated to reflect differences of >10%.

Eighteen test cultures containing green or purple photosynthetic bacteria as described above were prepared via the inoculation of washed cells obtained from stock cultures into experimental media containing 2 mM DBT with or without reduced inorganic sulfur. Controls grown in medium lacking DBT were included in these secondary tests. All cultures were incubated at 26° C in the light, under a headspace containing 0.03% CO₂ in N₂, for 14 d. Atmospheric levels of carbon dioxide were included in the system to permit autotrophic growth but also to allow detection of heterotrophic utilization of DBT. Growth was quantified visually on day 14. Cultures were then extracted twice with an equal volume of methylene chloride and metabolic products were analyzed by thin layer chromatography.

All cultures grew in the presence of DBT as a cometabolic substrate under these conditions (Table 4). However, DBT was clearly toxic to the green sulfur bacteria. A correspondingly small amount of biomass was produced in medium containing DBT as sole electron donor, suggesting that H₂ had been utilized as reductant in the prior work. Five of the eight cultures exhibited putative, weak DBT-reducing activity. In contrast, the purple sulfur bacteria grew well in the presence of DBT, indicating that DBT was not toxic to these cultures. These cultures also grew well in medium containing DBT as sole electron donor. Minimal heterotrophic utilization of DBT was observed. These findings suggest that these cultures reduce DBT but are incapable of assimilating carbon from this source. The purple nonsulfur bacteria grew well in the presence of DBT, indicating an absence of toxicity. The cultures grew as well in medium containing DBT as sole source of organic carbon as they did in standard medium containing ethanol and malate, suggesting that DBT was extensively degraded. This regime resulted in an enrichment for photosynthetic consortium members at the expense of nonphotosynthetic malate- or ethanol-utilizing organisms also present in the inoculum. However, the photosynthetic consortium members were apparently able to utilize carbon from DBT. The ability of the mixed culture to utilize sulfur from DBT was not assessed.

Chromatographic analysis of cultures of purple and green bacteria grown with DBT in the absence of H₂ indicated that many cultures were again capable of converting DBT to polar products with chromatographic behavior similar to that of DBT sulfone (Table 5).

Table 4. Effect of DBT on growth of anaerobic phototrophic bacteria ($N_2:CO_2$ atmosphere).^a

Culture	Control (no DBT)	Nutritional regime (DBT function)			
		Cometabolic substrate	Sole electron source	Sole organic carbon source	Sole electron and organic carbon source
Green sulfur bacteria					
A1	+++	++	+		
B1	+++	+	0		
C1	+++	+	+		
D1	+++	+	+		
E1	++++	++	+		
A2	+	+	0		
D2	++++	+	+		
E2	+	+	0		
Purple sulfur bacteria					
A3	+++	++	+	+	+
B3	++++	++++	+++	+	+
C3	+	++	+++	0	0
D3	+++	++++	++	+	0
E3	++++	+++	+++	+	+
Purple non-sulfur bacteria					
A4	++++	++++		++++	
B4	++++	++		++++	
C4	+++	+++		++++	
D4	+++	+++		++++	
E4	++++	+++		++++	

^a Growth estimated by visual inspection on day 14: 0, none; +, poor; ++, average; +++, good; +++++, excellent.

Table 5. Thin-layer chromatographic analysis of extracts of anaerobic phototrophic cultures containing DBT ($N_2:CO_2$ atmosphere).^a

Sample/Culture	Condition	R ^f values ^b			
Standards					
Blank	N/A	.52			
DBT	N/A	.54			1.0
DBT sulfone	N/A	.53		.66	
Purple sulfur bacteria					
A3	cometabolism		.55		.99
			.61		
	sole S		.61		1.0
	sole C	.52	.57		.99
			.62		
sole S+C	.53	.61		1.0	
B3	cometabolism		.55	.63	1.0
	sole S		.62		1.0
	sole C	.53	.57		.99
			.61		
	sole S+C	.54	.59	.65	.99
C3	cometabolism			.67	1.0
	sole S	.54	.58	.63	1.0
	sole C		.58		.99
			.60		
	sole S+C		.58	.63	1.0
D3	cometabolism	.53		.65	1.0
	sole S	.52	.57	.64	.99
	sole C		.55		1.0
	sole S+C		.59	.63	1.0
E3	cometabolism		.55	.64	1.0
	sole S	.54		.63	1.0
	sole C		.60		1.0
	sole S+C		.59		1.0

^a Immobile phase: silica. Mobile phase: acetone:heptane (1:1).

^b R_f values were tabulated to reflect differences of $\geq 5\%$.

These products again were nonfluorescent and were not susceptible to oxidative browning and thus appeared to be distinct from DBT sulfone and 1,1'-dihydroxybiphenyl. However, the oxidizable nonpolar product detected in the early experiment was not observed. Overall, significantly fewer polar products and significantly more products with mobility similar to that of DBT sulfone were formed in the absence of H₂ and at low (0.03%) CO₂ concentrations than under the conditions described previously (5% H₂, 5% CO₂). The identity of these products will be determined.

Cumulative results indicate that DBT is a potential source of sulfur and/or carbon for growth of anaerobic phototrophs. More important, these experiments confirm that DBT can serve as an electron donor for growth via sulfur-based anoxygenic photosynthesis. This work is the first report of oxidative metabolism of a "fossil" compound or of a sulfur heterocycle by anoxygenic phototrophic bacteria. These findings confirm that DBT is amenable to an oxidative microbial attack under anaerobiosis, with formation of polar products. The target of the biooxidative activity, i.e., the sulfur atom or the aromatic rings, has not yet been identified. Subsequent efforts are best aimed at characterization of DBT-reducing activity in purple sulfur bacteria due to their apparent resistance to DBT toxicity, high metabolic flux, and inability to assimilate ring carbon.

References

1. Aaronson, S. 1989. Enrichment Culture. In *Practical Handbook of Microbiology*, W. M. O'Leary, ed. CRC Press, Boca Raton. pp. 337-348.

Future Work

Products generated by anaerobic microbial attack on DBT will be analyzed. The range of sulfur-containing substrates susceptible to attack (other thiophenes, thiols, thioesters, etc.) will be determined. Pathways for anaerobic degradation of DBT will be developed. Completion of this work will form a secondary focus of planned activities.

A new initiative, targeting the development of microbial cultures capable of removing organic nitrogen from coal and/or coal-derived substances, will be the primary focus of experimental efforts during the remainder of FY 1993.

4.2 ADVANCED BIOREACTOR SYSTEMS

T. C. Scott

Advanced bioprocessing concepts can play an important role in coal utilization and conversion. This R&D program is aimed at elucidating the fundamental mechanisms that are important in appropriate bioprocessing concepts or coal interactions, particularly those that have potential generic impacts. Further, the program will be a collaborative partnership of ORNL with academic and industrial researchers.

To obtain the high throughput and low inventory needed for large-scale bioprocessing of coal, a new family of advanced bioreactor systems will have to be developed. The focus of the research in this area will be on continuous columnar bioreactors which have the potential for carrying out three-phase operations. Although both fixed and fluidized bed bioreactors will be studied, the initial work will be on liquid-solid fluidized bed systems and aqueous-liquid-solid fluidized bed systems for direct biological interactions with extremely small coal particles.

ORNL RESEARCH

In order to effectively describe and predict column performance for polydisperse particle systems, experimental information is needed in four vital areas: (1) axial pressure drop, (2) particle size distribution as a function of axial position, (3) dispersion characteristics of the liquid phase, and (4) dispersion characteristics of the particles. During the last reporting period work has concentrated on the second of these four issues: in situ measurement of particle size distributions.

Effective reactor modeling, design, and implementation rely upon knowledge of bed expansion and segregation tendencies with particles of varying size and density. Last quarter we demonstrated a fluorescence method for the direct observation of coal particles in a liquid fluidized bed reactor. In this method, the dye fluorescein is added to the liquid phase and serves as a contrast agent. A modified fluorescence microscope abuts the column and is used to image the fluorescence emission in response to epi-illumination (see Figure 1). The

Fig. 1. Schematic of fluorescence method for the study of liquid fluidized beds of solid particles. (1) fluidized bed column, (2) dispersed phase, (3) continuous phase, (4) fluid reservoir, (5) pump, (6) light source, (7) microscope, (8) objective, (9) fluorescence filter set (hand pass filter, dichroic mirror, and long pass filter), (10) video camera, (11) mobility of optical platform for focus and height adjustment, (12) observer, (13) VCR, (14) frame grabber/analysis computer.

resulting image (dark particles on a bright field of fluorescent liquid) may be digitized and analyzed using edge detection algorithms to provide particle area fraction and size distributions. The microscope may be positioned at any height relative to the column, thus producing particle segregation and expansion statistics as a function of bed height. Unlike previous attempts to visualize segregation in fluidized beds which require direct sampling, use of a modified ultra-thin column, low particle volume fraction, or radiation, the proposed method is non-invasive and may be conducted in an operational reactor at standard flow rates and particle loading. Further, unlike our previous attempts to directly label a bimodal distribution of coal particles, the current method may be applied to any distribution of particle sizes and densities, without possible alteration of particle hydrodynamics.

We demonstrated the ability to obtain video images of individual particles in a liquid fluidized bed of coal. Efforts this quarter have identified the digital filtering and sizing algorithms necessary to convert such images into size distribution histograms. The optical platform has been calibrated to enable direct size measurement in the presence of optical distortion, the glass column reconstructed for easier operation, the system demonstrated in a larger scale reactor, and coal sieved to the desired size in sufficient quantities for segregation experiments to begin.

Once video images of coal in a fluidized bed are obtained through the use of fluorescence microscopy, they must be processed before they may yield quantitative size information. A "watershed" digital filter is applied to the image in order to enhance the morphological features of the image. Grey level thresholding is utilized to detect object edges, and information is then available of particle size in terms of number of video picture elements (pixels). We have calibrated the optical train in order to provide a relationship between pixel size and real object size in microns. This calibration also accounts for slight optical distortion due to the curvature of the glass column. To arrive at this relationship, glass micrometer slides were fixed onto the inside surface of the reactor column and the column was filled with water. One slide was placed horizontally and the other vertically, with respect to the column. The micrometer rulings were imaged using the fluorescence optical system, and the number of pixels corresponding to a known distance in the horizontal and

vertical directions was measured. This allowed for size distribution histograms to be constructed from the preliminary scanning experiment described last quarter (see Figure 2).

The next goal in our study of segregation in the fluidized bed reactor is the experimental verification of the accuracy of the fluorescence imaging technique. In these experiments, a bimodal distribution of coal particles will be fluidized at conditions such that the particles will not segregate. The fluorescence technique's accuracy will be assessed by its ability to report constant particle size distributions as a function of bed height in this non-segregating bed. The reported size distribution will also be compared to the known quantities and sizes added to the bed. Following these verification studies, investigations of segregating regimes will begin.

In preparation for this next series of experiments, the 4 ft glass reactor used in previous fluidized bed experiments was reconstructed to allow for greater experimental flexibility in performing pressure drop measurements. The ability of the fluorescence technique to obtain images in the taller column at realistic coal loading and flow rates has also been verified (see Figure 3). Finally, bituminous Illinois No. 6 coal has been wet sieved to the desired size fractions in sufficient quantities for a series of segregation experiments to be performed. Validation and segregation experiments have just been initiated. The data obtained from such studies will be of use in the development and verification of predictive mathematical models of fluidized bed expansion and segregation.

Future Work

The primary focus of the next quarter of work will be on obtaining particle-size distributions for bimodal mixtures of coal particles in the 30-125 μm regime. The fluorescence microscopy technique will be used to make these measurements for comparison to the model developed in concert with Washington State University.

Fig. 2. Histograms of particle major axis size as a function of bed height. As reported last quarter, a mixture of 53 - 63 mm and 150 - 250 mm screen sized coal was fluidized and the fluorescence imaging method used to record images at bed heights of 1, 3.5 and 10 cm above the bed distributor. As can be seen, the lower section of the bed (1 cm) contains both large and small particles, whereas the upper section contains only smaller particles. This type of information will allow the investigation of particle segregation in fluidized beds. Note that the major axis size does not necessarily correspond to the screened size, since the screen size is more closely a measure of minimum aspect size.

Fig. 3. Fluorescence image of coal fluidized in the 4 ft columnar reactor. The solids volume fraction was near 45%, and the superficial liquid flow rate was 0.015 cm/sec. Coal particles appear dark on the bright fluorescent field of liquid.

ADVANCED BIOREACTOR MODELING

Introduction

The on-going research at Washington State University is primarily oriented toward developing a predictive model to accurately describe the hydrodynamics of the fluidized bed bioreactor for coal biosolubilization. These bioreactors exhibit hydrodynamic characteristics which are entirely different from the conventional fluidized-bed bioreactors. This is due to the fact that the progressive solubilization of coal with time leads to a situation where coal particles of widely varying diameters will be present in the fluidized bed. Moreover, as the particle size decreases due to the solubilization, the equilibrium of forces acting on the solid particle shifts in such a way as to impart an upward tendency of movement in the fluidized suspension. Ultimately, the coal particles which have been being solubilized will start to elutriate from the bed. This elutriation will start when the liquid superficial velocity exceeds the terminal velocity of the particles. These phenomena make the process of coal biosolubilization in a liquid fluidized bed inherently dynamic in nature. As a result, the hydrodynamics of such a reaction configuration can not be confidently described using conventional fluidized bed modeling techniques. At the same time, there is, unfortunately, not much information available in the literature which addresses the peculiarities of the situation at hand.

As a part of our on-going research to characterize the fluidized-bed hydrodynamics, we have been successful in developing a dynamic mass-conservative model to describe the particle concentration distribution in the coal fluidized bed. Once the concentration distribution of solid particles is known, the bed voidage fraction and its bulk density can be easily computed. The main features of this model were described in the last report. During this present quarter, the research proceeded along the same lines with an emphasis on enhancing the predictive capability of the model. In this context, necessary modifications were made in the model to incorporate the ever-changing dynamics of the bed due to elutriation of coal particles.

Another major task of key importance that was accomplished in the present quarter was the development of the form which a realistic correlation for predicting the dispersion coefficient of the solid particles in the fluidized-bed must assume. An accurate prediction of the particle mixing tendency is crucial for successful preliminary design and subsequent scale-up of a liquid fluidized bed bioreactor. This issue assumes added importance in the present context where particles of different size are present together in the fluidized bed. In the following, we intend to dwell on this subject a little further.

Correlation for the Prediction of Particle Dispersion Coefficient

The measurement of particle dispersion tendency gained attention of the researchers as early as the sixties due to its role in influencing fluidized-bed hydrodynamics.^{1,2} Even today this topic continues to be actively pursued by workers interested in different aspects of fluidized-bed hydrodynamics. However, our main interest is to examine how the particle dispersion coefficients affect the mixing and segregation tendencies of coal fluidized bed containing coal particles of different sizes. Despite significant work in this area, there are not many correlations reported in the literature. These correlations will be briefly discussed next.

Dorgelo et al.³ proposed the following relationship for the prediction of the particle dispersion coefficient in a liquid fluidized bed,

$$D_i = 0.1 U_o^2 \quad (1)$$

$$\text{For} \quad 1.0 \times 10^{-3} < U_o < 1.0 \quad (2)$$

Here, D_i is the dispersion coefficient with units $\text{m}^2\text{-s}^{-1}$, and U_o (m-s^{-1}) is the liquid superficial velocity. Note that this equation uses no dimensionless groups, and so extensions to regions outside the range of experimental measurements are dubious, at best.

Recently, Kang et al.⁴ proposed a similar correlation which is given by

$$D_i = 2.97 \times 10^{-3} (U_o + U_{mf})^{0.802} \quad (3)$$

where, U_{mf} is the minimum fluidization velocity of the particles of species i . All the quantities in the above equation have units in MKS system. Again, no dimensionless groups are used.

It is obvious from equations (1) and (3) that both correlations show a strong relationship between the particle dispersion coefficient and the liquid velocity. However, the correlation of Dorgelo et al.³ shows a much more pronounced dependence of particle mixing characteristic on the liquid velocity. Another difference between the two correlations is the presence of minimum fluidization velocity term in the correlation of Kang et al.⁴

It is worthwhile to note that these correlations suggest a strong dependence of the particle dispersion coefficient on the liquid superficial velocity, but ignore the effect of other important fluid and particle properties thereby limiting their applicability. For example, these correlations will erroneously predict identical values of the dispersion coefficients for both the large and small particle species in a liquid fluidized bed irrespective of their size difference. Therefore, there is a need of developing a suitable correlation based on dimensionless parameters capable of appropriately describing the influence of important system variables on the particle dispersion characteristics. A review of the literature on the subject of fluidized beds would suggest the use of the following dimensionless parameters,

$$Pe = \frac{U_o d_p}{D}; \quad \frac{U_o}{U_t}; \quad Fr = \frac{Re^2}{Ga} = \frac{\rho_f}{\rho_p - \rho_f} \frac{U_o^2}{g d_p} \quad (4)$$

Here, Fr is the two-phase Froude number, Re is the Reynolds number and Ga is the Galileo number.

Note that the Galileo number is the ratio of buoyancy and viscous forces whereas the Reynolds number is the ratio of inertial forces to viscous forces. These two dimensionless numbers are combined to give rise to another dimensionless number which is very similar to the Froude number except the fact that the denominator, instead of being the gravitational force alone, is the difference of gravitational and buoyancy forces. This is, therefore, often termed as the two-phase Froude number owing to the presence of two phases.

Due to the lack of the availability of experimental data on the mixing characteristics of small low density coal particles (a problem being addressed in Section 1 of this report), the experimental results of Juma and Richardson (1983) were processed as described by Asif and

Petersen in an article which was recently submitted for publication. They found that the dispersion coefficient for both the large and small particles can best be correlated using the following form of expression

$$\frac{Fr}{Pe} = K_1 \left(\frac{U_o}{U_i} \right)^{K_2} \quad (5)$$

For the experimental data of Juma and Richardson (1983), $K_1=7.28$ and $K_2=1.97$, the correlation coefficient was found to be 0.925 with a 13.5% standard error of prediction. This correlation is applicable over the following broad range,

$$6.0 \leq Re \leq 10^3; \quad 0.5 \leq \epsilon \leq 0.92; \quad 1.4 \times 10^{-2} \leq Fr \leq 1.7$$

Note that the equation (5) correlates the particle dispersion coefficients in terms of dimensionless numbers. This feature ensures the applicability of the correlation to fit a wide variety of situations of practical interest. Furthermore, the two parameters of the model introduce a greater degree of flexibility in the correlation, and probably would need to be adjusted for coal fluidized beds in light of experimental results. However, we emphasize that the form of the correlation accounts for the forces acting on the particle, and we expect that this form will be applicable for coal particles.

Further Developments in the Modeling Studies

Since we are interested in describing the dynamics of the coal fluidized bed with elutriating particles, the appropriate relationship for computing the fluid interstitial velocity, in this case, is given by

$$U_f = U_o + C_{s_i} U_{r_i} \quad (6)$$

where, U_f is the fluid interstitial velocity, U_n is the particle velocity relative to the fluid, U_o is the fluid superficial velocity, and C_{si} is the volume fraction of the solid particles of species i .

Another modification was made in the model to account for the mass out-flow from the bed due to the elutriation of particles when the fluid velocity exceeds their terminal velocity. In this case, the boundary condition at the top of the bed is given by

$$(J_i)_L = (U_{pi} C_{si})_L \quad (7)$$

where, J_i is the mass flux of species i , U_{pi} its velocity relative to the stationary observer and C_{si} is its volume fraction. Here, L indicates the top of the fluidized bed of height L .

Results and Discussion

Figure 4 shows the development of the total particle concentration profile with time when the liquid superficial velocity is increased from 0.015 to 0.033 cm/s for $D_i=0.5 \text{ cm}^2/\text{s}$. Note that none of the particle species will elutriate at 0.015 cm/s. But, at a liquid velocity of 0.033 cm/s, particles with a diameter less than 46 microns will start to elutriate from the coal fluidized bed under study which contains 17 coal particle species in the range of 34.5 - 74.5 microns diameter. The figure shows that the particle concentration decreases dramatically in the lower-bed regions as the bed expands. As expected, the total particle concentration in the upper bed regions are always less than those prevailing in the lower bed regions. However, the time evolution of the particle concentration profile at the top of the bed exhibits interesting behavior. As the time progresses, the total particle concentration increases as shown by the point A on the plot and then slowly decrease. This increase in particle concentration at the top of the bed is due to the influx of small diameter elutriating coal particles. As more and more small particles leave the bed, the total particle concentration profile again shows a decrease.

Figure 5 shows the influence of particle dispersion coefficient on the particle elutriation in the fluidized bed. In this case, the dispersion coefficient is $0.2 \text{ cm}^2/\text{s}$ as against the previous case of $0.5 \text{ cm}^2/\text{s}$, but all other conditions are the same as in Figure 4. It is

Fig. 4. Development of total particles concentration profile with time along the bed height ($U_o = 0.033$ cm/s, $D_i = 0.5$ cm²/s).

Fig. 5. Development of total particles concentration profile with time along the bed height ($U_o = 0.033$ cm/s, $D_i = 0.2$ cm²/s).

Fig. 6. Influence of particle dispersion coefficient on the prediction of fluidized-bed height based on particle concentration distribution model.

evident from Figure 5 that the rate of particle elutriation is much higher at low values of particle dispersion coefficients so that the system attains the steady state rather quickly. This behavior of the fluidized bed to exhibit slower dynamics at low values of the particle dispersion coefficients is very interesting, and can be exploited, in conjunction with appropriate dynamic experiments, to quantify the solids mixing tendency in the fluidized bed.

Figure 6 shows the dependence of the total bed height on the particle dispersion coefficient when the particle concentration distribution model is employed. Note that this model is based on the particle transport by convection and dispersion mechanisms. Increasing the particle dispersion, therefore, predicts a similar increase in the bed height. The prediction of the serial-bed model as proposed by Epstein et al.⁵ is also shown in this figure. It can be seen that prediction of this latter model is independent of particle dispersion or mixing tendency. At present, it appears that this issue needs to be further explored and a combination of the aforementioned two approaches might provide a better estimate of the expansion characteristics of the fluidized bed.

Future Work

The primary focus of the next quarter will be to incorporate the kinetics of solubilization in the modeling equations and to examine its effect on the rate of elutriation of coal particles from the fluidized bed.

The proposed correlation for the prediction of the particle dispersion coefficient will be tested in the light of experimental data available from ORNL.

Other Activities

During this quarter, an article entitled "Liquid Fluidization of a Binary Mixture of Solid Particles" was submitted for publication in the AIChE Journal. Referees comments were received and were generally quite favorable. With necessary modifications, the paper was resubmitted to the Editor.

Up to 50 hours of supercomputer time were approved on the CRAY computer at the UNLV Supercomputer Center in support of this project. Efforts are being made to obtain

access to this time, and to begin to use this resource. Use of this facility should significantly enhance this project, as we are reaching the limits of our departmental VAX computer on this project.

Dr. James Petersen and M. Asif are undertaking a visit to ORNL in connection with discussing, and possibly implementing, new strategies for modeling the coal solubilization process.

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4.3 BIOCONVERSION OF COAL

C. D. Scott

This program has examined the feasibility of using biological catalysts for the conversion of coal to useful liquid fuels. Biological reagents potentially useful in this application include intact microorganisms in pure or mixed culture and isolated enzymes. The current emphasis is on the investigation of the use of chemically modified enzymes in organic media to enhance liquefaction/solubilization of coal.

RESEARCH RESULTS

Further progress has been made in the enzymatic enhancement of the conversion of coal to liquids. The primary emphasis has been on enzyme-enhanced reduction of a model compound and the continued evaluation of thermophilic hydrogenases.

Biocatalysts

The two reducing enzymes previously used in this program, a hydrogenase isolated from *Proteus vulgaris* and cytochrome c purchased from Sigma Chemical Co., are continuing to be evaluated but additional work has been carried out on three thermophilic hydrogenases. A small subcontract has been executed with the University of Georgia for Professor M. W. W. Adams to supply us with crude hydrogenase extracts from two hyperthermophiles, *Pyrococcus furiosus* and an unclassified bacterium, ES-4. The former is a Ni-Fe hydrogenase that is expected to be relatively stable in air while the latter is a Fe-only hydrogenase that is very active but which is likely sensitive to inactivation in air.^{1,3} The hydrogenases from these super thermophiles have been shown to be stable at temperatures greater than 80°C. A hydrogenase from *Azotobacter vinelandii* obtained from Dr. Howard Adler, Oak Ridge Associated Universities, has also been available in small quantities. It is expected to be active up to 60°C.

To use these enzymes in organic solvents, it is necessary to chemically modify them to increase their hydrophobicity. In the recent past, dinitrofluorobenzene (DNFB) has been used to add dinitrophenyl groups to the enzymes. In addition to that approach, two types of activated polyethylene glycol (PEG) have also now been tested for enzyme modification. These are PEG activated with cyanuric chloride (PEG-c) and PEG activated with p-nitrophenyl carbonate (PEG-n). Both of these materials were obtained from Sigma Chemical Co. The techniques used for this type of enzyme modification, which were developed in the AR&TD program entitled "Fundamental Bioprocessing Research for Coal Applications," are described in a recent publication and the current quarterly progress report for that program.^{4,5}

Organic Solvents

Two organic solvents and a solvent mixture have continued to be used for tests with a model compound and for coal conversion. These include pyridine to allow study of the effects of a relatively polar solvent, benzene for studying the effects of a relatively nonpolar solvent, and a solvent mixture that is used to simulate a process-derived solvent (45% tetralin, 40% 2-methylnaphthalene, and 15% p-cresol).

Tests with a Model Compound

At the suggestion of Dr. M. Farcasiu of the Pittsburgh Energy Technology Center, the model compound, 1-[4-(2-Phenylethyl)benzyl]naphthalene (PBN, obtained from TCI America) is being used in order to allow the study of the hydrogen reduction mechanisms that may be occurring within the coal structure. Since coal is a very complex structure, model compounds such as this one that contain chemical structures somewhat similar to some of those found in coal, can be used to determine specific chemical interactions that are catalyzed by the enzyme systems.

PBN is a naphthyl group connected to bibenzyl by a methyl group. Reduction reactions could result in splitting off the naphthalene or a methyl derivative of naphthalene leaving a bibenzyl molecule, splitting off a benzene, toluene, or xylene molecule, splitting one

of the ring compounds, and other combinations. Analysis for the model compound and possible reduction products were made by a gas chromatograph (GC) using the techniques described in the last quarterly report.⁶ GC retention times were determined for the model compound in the solvent of interest and for many possible reduction products (See Fig. 1).

Tests were made in shake flasks at controlled temperatures with about 10 mL of the liquid mixture that contained 1 mg/mL of PBN and 1- to 4-mg/mL of modified hydrogenase and/or cytochrome c. It was also found to be useful to include 1 mg/mL dodecane as a nonreactive internal standard. Since higher temperatures were used in some tests, 50 mL sealed shake flasks (serum bottles sealed with a septum) were used in order to decrease the vaporization rate of the solvents. Prior to sealing the bottles, the head space was sparged with hydrogen gas for 30 min. These sealed bottles were temperature-controlled in a fluid bath with gyratory shaking at 120 rpm during a 24-h period. The concentration of PBN and reduction products were determined periodically by the removal of 1 mL samples through the septum that were then injected into the GC.

Hydrogenase from *P. vulgaris* - It has been previously demonstrated that DNFB-modified hydrogenase from *P. vulgaris* or in combination with DNFB-modified cytochrome c, did not appear to effect the model compound in benzene during a 24-h period.⁶ However, in pyridine there was an apparent small loss of the model compound over the 24 h of the test when the modified hydrogenase was present and an apparent 13% loss when both modified hydrogenase and modified cytochrome c were present. In the latter case, small quantities of breakdown products were also detected that had GC retention times similar to those of toluene and bibenzyl.

Several additional tests were made with this enzyme mixture in which DNFB and PEG-n were used as the modification reagents. There was no apparent interaction with the model compound in p-cresol, benzene, or the synthetic process-derived solvent.

Hydrogenase from *A. vinelandii* - It was found that when modified, this enzyme had very low activity (<.01 units/mL); therefore, it was not investigated for reducing the model compound.

Hydrogenase from Bacterium, ES-4 - This enzyme was found to have severe inhibition when exposed to air. To date, the operating conditions that have been used for chemical

Fig. 1. GC retention times of model compound (PBN) and possible reduction products with a comparison of experimentally-determined reduction products. Operating conditions were described in ref. 6.

modification of the enzyme have resulted in such inactivation. As a result, It was not investigated for interaction with the model compound, but as better experimental techniques are developed, this enzyme will also be tested.

Hydrogenase from *P. furiosus* - As in the previous scouting tests, the most successful results for the enzyme-enhanced reduction of the model compound were from tests with 2-4 mg/mL of hydrogenase from *P. furiosus* mixed with 2-4 mg/mL of cytochrome c. In order to also show the effects of both polar and nonpolar solvents, either pyridine or benzene were used in these tests. There were apparent reductions in PBN concentration in either of these solvents.

Three chemical reagents were tested for chemical modification of the enzymes, DNFB, PEG-c, and PEG-n. It was found that there was apparent interaction with the PBN with all three of these modification techniques, but the most significant reduction of model compound concentration was when the enzymes were modified with PEG-n. This reagent also had the least deleterious effect on enzyme activity. The best results were obtained with a mixture of these modified enzymes in pyridine where the concentration of PBN was decreased by 37.6% at 50°C. There did appear to be a temperature effect. For example, with benzene as the solvent and the same mixture of enzymes, there was an apparent enhancement from 30 to 50°C but an apparent decrease at 75°C with the maximum conversion of the model compound being 21.7% (See Table 1).

Apparent reduction products were detected, in all cases where the PBN loss exceeded 5%. Typically these included material with a GC retention time similar to bibenzyl and at least three other components with higher retention times and presumably higher molecular weights (Fig. 1). As previously suggested, the reductive degradation of the model compound appears to be primarily due to splitting at the methyl bridging, although other interactions are obviously taking place as well. In this case, only benzene was evaluated as the solvent using the same experimental conditions indicated above.

Table 1. Enhanced conversion of the model compound with PEG-n modified hydrogenase from *P. furiosus* mixed with PEG-n-cytochrome c in benzene

Temperature (°C)	% Conversion of Model Compound
30	18.0
50	21.7
75	5.0

Other Reducing Agents - It has previously been shown that molecular hydrogen can be used as the reducing agent in the enzyme-enhanced conversion of coal to liquids. However, reduced cytochrome c also can contribute to the enhancement of this type of interaction. There is an indication that the reduced cytochrome c is actually a hydrogen donor or reducing agent itself, although it might also serve as an important electron transport compound as well. Other less expensive reducing agents are also of interest especially when an integrated processing system will be considered. We are beginning to study possible organic reducing agents for this purpose.

There was no indication that tetralin, a well known hydrogen donor, has an effect that can be used for enzyme-enhanced coal conversion. However, preliminary results with dithiothreitol (DTT, obtained from Sigma Chemical Co.) indicate that it may have some utility for this purpose. DTT is soluble in a wide range of organic solvents and is a known reducing agent that is frequently used in biochemical experiments. It has now been shown to reduce cytochrome c in both aqueous and organic media with complete reduction occurring in about 5 min. This compound and others will continue to be studied as reducing agents for this application.

Coal Conversion Tests

Although the major emphasis during this period was on investigating new biocatalysts and on biocatalytic reduction of a model compound, some tests were also carried out on the conversion of Illinois No. 6 bituminous coal in shake containers using techniques previously described.⁴⁵ The most important of these was a test with Illinois No. 6 bituminous coal in a sealed shake bottle that included a mixture of PEG-n- hydrogenase (from *P. furiosus*) and PEG-n-cytochrome c. In tests made at 30°C, it was demonstrated that there was a considerable enhancement of coal conversion (See Fig. 2) with 15.9% of the coal being converted in the presence of the enzyme but only 7.3% being solubilized with benzene alone. This is among the best results obtained with benzene and again demonstrates that the thermophilic enzyme from *P. furiosus* shows great promise.

Future Work

Work will continue on the reduction of the model compound with an attempt to increase the degree of degradation. Thermophilic enzymes will continue to be explored and a broader temperature range will be more thoroughly explored. Alternative reducing agents will be studied and more emphasis will be placed on use of the synthetic process-derived solvent. Coal conversion tests will continue to be made with the best biocatalytic conditions that are established from the other studies.

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Fig. 2. Conversion of Illinois No. 6 bituminous coal to liquids enhanced with PEG-n-modified hydrogenase from *P. furiosus* and cytochrome c in a sealed shake container with an atmosphere of molecular hydrogen at 30°C.

4.4 RENEWABLE HYDROGEN PRODUCTION FOR FOSSIL FUEL

E. Greenbaum and S.L. Blankinship

This program is focused on the production of molecular hydrogen and oxygen by light-activated microalgal water splitting. Molecular hydrogen is an extremely valuable chemical feedstock and fuel. The object of the research is to understand the kinetics and mechanism of photosynthetic hydrogen production so that a real-world engineering system can be constructed. Hydrogen has important applications in coal liquefaction and gasification.

4.4.1 Background

Although carbon dioxide is the terminal electron acceptor of normal photosynthesis, other electron acceptors are possible. In particular, in their pioneering work, Gaffron and Rubin showed that the enzyme hydrogenase can catalyze the photoevolution of molecular hydrogen in a dinitrogen atmosphere.¹ Anaerobiosis (e.g., atmospheres of nitrogen or helium) is, from a physiological point of view, an unusual condition. However, it can be used to study the question of alternate fates of photosynthetic reductant—in particular, the branching ratios between hydrogen evolution and carbon dioxide assimilation using water as the source of reductant. This paper focuses on an understanding of partitioning photosynthetic reductant in the context of absolute rates of photosynthetic electron transport.

Gaffron and Rubin first showed that green algae (such as *Scenedesmus*) could liberate hydrogen gas in light, provided the algae remained under CO₂-free anaerobic conditions.¹ Further investigations indicated that the simultaneous photoevolution of oxygen and hydrogen from water is qualitatively analogous to normal photosynthesis in that the bulk of reductant is provided by water splitting.^{2,3} When such algae are exposed to light, the water-splitting complex of Photosystem II (PS II) provides reducing equivalents for the photoproduction of molecular hydrogen (catalyzed by hydrogenase), instead of carbon fixation. *Chlamydomonas reinhardtii* is another algal species that possesses the ability to perform biophotolysis of water.^{4,5,6,7}

Previous studies have shown the importance of a bicarbonate effect on the rate of photosynthetic electron transport (PET) or oxygen-evolving ability.^{8,9} Warburg and Krippahl first observed this effect,¹⁰ and it has been studied further by Stemler and Govindjee.¹¹ In general, normal rates of electron transport in plants require bicarbonate (or dissolved CO₂).^{12,13}

At the same time, of course, CO_2 is the key reagent of the Calvin cycle as the terminal electron acceptor and activator of crucial enzymes.¹⁴ Under anaerobiosis, the Calvin cycle competes with hydrogenase for electrons activated by Photosystems I and II (PS I and II) and overwhelms it when high amounts of CO_2 (1% in helium) are present.⁶ By titrating the CO_2 concentration in an algal environment, a value was sought such that enough inorganic CO_2 would be present to maintain relatively high PET rates while restricting supply of the basic reagent of the Calvin cycle. The key concept here is based on differences in the level of bicarbonate required for binding to Photosystem II versus its utilization in the Calvin cycle. With the Calvin cycle suppressed under low bicarbonate, reductant from water should favor the H_2 -forming pathway. Using this approach, conditions were obtained for improved hydrogen yields in *Chlamydomonas reinhardtii*. It clearly illustrates that control of atmospheric carbon dioxide concentrations is a rational approach to improving the partitioning of energy from water splitting into hydrogen production in algae.

4.4.2 Materials and Methods

Chlamydomonas reinhardtii, strain 125 (from the University of Texas Culture Collection, Austin, TX) was grown in a liquid minimal medium with 125-rpm shaking in a 30°C water bath under continuous illumination provided by a 500-W incandescent bulb. Each experiment used 5 mL of algal suspension containing roughly 0.1-mg chlorophyll. Chlorophyll (Chl) concentrations at the end of each trial were determined by measuring the absorbance of methanol extracts.¹⁵

The experimental apparatus is illustrated schematically in Fig. 1. Gas mixtures were blended using ultra-high purity helium (Alphagaz, Morrisville, PA) and a standard (either 350 or 20 ppm CO_2 in He, Matheson Gas Products, Inc., Morrow, GA). Each of the cylinders was connected on MKS Type 1258B mass flow meter and controlled by a MKS Type 260 controller. By diluting a controlled flow rate of standard with a controlled rate of pure helium (for a total rate of 50 mL/min), the digital flow system could provide the desired CO_2 concentration. This gas mixture then bubbled through the algal suspension (5 mL in a reaction vessel) to maintain anaerobiosis and constant CO_2 concentration, as well as to carry any evolved gases to the detectors downstream.

Varying illumination levels of the algal vessel were provided by a programmable Kepco power supply. This varied the voltage to a 250-W, 24-V projector bulb (GTE Products Corp., Salem, MA). Intensities used were: 227, 130, 64, 24, 5.3, 2.4, and 0.1 W m^{-2} ,

Fig. 1. Apparatus for measurement of hydrogen and oxygen photoproduction by algae. The solid arrow depicts the continuous gas flow through the system. A compressed helium source and a carbon dioxide standard (in He) provide the carrier gas that continuously flows through the system. A circulating water bath (not shown) pumps 25°C water through a glass jacket surrounding the reaction vessel to maintain constant temperature. One microcomputer (HP-85) handles the experimental parameters of light level, CO₂ concentration, and calibration of detectors while another (IBM-compatible) records time along with oxygen- and hydrogen-sensor output. Both computers communicate to their respective instruments via IEEE-488 interfaces.

respectively (photosynthetically active radiation, PAR), as measured with an EG&G Model 550 Radiometer/photometer and Schott cut-off filters (RG695, GG420). Light intensities occurred at 1.5-hour-on and 1-hour-off cycles in the above irradiation sequence for each experiment after a minimum 3-hour incubation in darkness.

Oxygen was measured by a Hersch galvanic cell¹⁶ and hydrogen by a tin oxide (SnO_2) gas-sensing semiconductor.¹⁷ Current and voltage from the O_2 and H_2 detectors were read by Keithley digital multimeters, which directed their outputs to an IBM-compatible computer through the IEEE-488 interface. The personal computer digitally recorded the data (time and detector readings) on the hard disk drive for subsequent processing and analysis. Another microcomputer, an HP-85 with IEEE-488 interface, programmed the gas-flow controller, power supply (for light output), and the current source (for calibration).

For calibration of the gas sensors, a Keithley Model 220 current source (Keithley Instruments Inc., Cleveland, OH) generated electrolysis currents in discrete steps of current: 100, 75, 50, 25, 15, 10, 5, and 0 μA . These currents corresponded to known rates of gas production by Faraday's Law of Electrochemical Equivalence ($1 \mu\text{A} = 9.33 \text{ nmol } \text{O}_2/\text{h} = 18.66 \text{ nmol } \text{H}_2/\text{h}$). A rectangular hyperbola, $y = ax/(1 + bx)$, was used to fit applied current (x) to the hydrogen sensor response (y). The parameters a and b were adjustable, and they were determined by a least-squares error fitting routine. For oxygen, the sensor response (y) exhibited a linear relationship with the applied current (x): $y = ax + b$ (fitted by linear regression). Using these calibration curves, detector response during the light reactions could be translated to current or rate of gas evolution.

Temperature for all experiments remained at 25°C through a heated circulating water bath connected to the jacketed vessel that contained the algae. To prevent leakage of gases, connections between the components were made with glass and brass O-ring fittings, spring clamps, and copper tubing.

4.4.3 Results and Discussion

Three different regimes of CO_2 concentrations (58, 30, and 0.8 ppm) and light intensities are presented in Fig. 2 showing rates of hydrogen and oxygen evolution versus time. The onset of light-activated hydrogen and oxygen photoproduction is evident as is their decline when the light is turned off. Dark hydrogen evolution is subsequently observed (a phenomenon described by Gaffron and Rubin, 1942 and amplified by Klein and Betz, 1978).

Fig. 2. Representative results of hydrogen (solid line) and oxygen (dashed line) evolution by *C. reinhardtii* at 58, 30, and 0.8 ppm carbon dioxide. A 2-hour calibration period preceded the actual light reactions, which started at the third hour. Seven cycles of 1.5-hour light and 1-hour dark were performed for each of the seven irradiances (in order, from left): 227, 130, 64, 25, 6.3, 2.4, and 0.1 $\text{W}\cdot\text{m}^{-2}$ ($\uparrow$ =light on, $\downarrow$ =light off). The peak areas, after background subtraction, represent yields of H_2 or O_2 , and first half-lives (the decay time from maximum rate to half-maximum) were compiled for hydrogen. Other experimental conditions are described in the text.

Using these data, one can obtain gas yields during light periods by integrating the peaks. For hydrogen profiles, the first half-life measures the time of decay from the maximum rate to half maximum. All yields were normalized to 1 mg of Chl by dividing by the amount of Chl present for each trial (usually 0.1 mg).

4.4.3.1 Lower CO₂ Concentrations Increase H₂ Yields

Figure 3 illustrates the results from 11 experiments at varying carbon dioxide levels and 130 W·m⁻² irradiance. This light level was chosen because it generated the highest oxygen yields at most of the CO₂ concentrations used without causing photoinhibition. Oxygen yields indicated the activity of water splitting, which supplied the bulk of reductant for hydrogen synthesis. The six other light intensities exhibited patterns similar to 130 W·m⁻². Fifty-eight ppm was the highest CO₂ concentration tested because 350 ppm CO₂, which is close to normal atmospheric levels, produced similar gas yields (data not shown). As the CO₂ levels for algae decreased, hydrogen yields climbed slowly, reaching a maximum at 0.8 ppm (11,360 nmol), where the Calvin cycle was impaired presumably because of insufficient CO₂ supply. At the other extreme, CO₂ levels greater than 30 ppm allowed the Calvin cycle to dominate so that there were only quick bursts of hydrogen production upon illumination. The noteworthy result is the highest yield of hydrogen was obtained at 0.8 ppm CO₂, rather than at 0 ppm CO₂ where the Calvin cycle would be totally deprived of external inorganic carbon.

4.4.3.2 Lower CO₂ Concentrations Inhibit H₂ Decay

Hydrogen rates peaked and declined in most of the 1.5-h light periods (see shape of H₂ peaks in Fig. 2). (The low light intensities are a notable exception.) First half-lives ($t_{1/2}$) indicated the duration of hydrogenase activity at various CO₂ concentrations (Fig. 4). These are not implied to be the half-lives of exponential decay. They reflect the real-time loss of light-activated hydrogenase activity, due to competition with the Calvin cycle and/or depletion of alternate donor reductant pools. No permanent damage to hydrogen-forming capacity resulted from this decline, as indicated by resurgent rates of hydrogen evolution during subsequent light periods. As displayed in Fig. 4, the decay is slowest at the 0.8 ppm CO₂ level, indicating that hydrogen photoproduction had its slowest decay at this level. The general trend showed first half-lives rising with decreasing CO₂ and roughly following the behavior of hydrogen yields.

Fig. 3. Algal photoproduction of hydrogen (■, dashed line) and oxygen (●, solid line) at various carbon dioxide levels. Shown are the trends of the gas yields (integration of peaks as in Fig. 2) for 1.5-hour light periods ($130 \text{ W} \cdot \text{m}^{-2}$ irradiance). All yields are normalized to 1 mg Chl. Of the eleven CO_2 levels tested, hydrogen production is greatest near 1 ppm, but oxygen yield at this point has dropped to 30% of the value at 58 ppm CO_2 .

Fig. 4. First half-lives of decay for hydrogen rates. These measure the time it takes for the maximum H_2 rate to decay to half-maximum. Shown here are the first-half-lives (●) for the $130 \text{ W} \cdot \text{m}^{-2}$ light level, taken from the data for Fig. 3, with a solid line as the "smooth fit" through the data. Since all the hydrogen rates experienced a notable decay from an initial burst, this half-life describes how sustained the hydrogenase activity of the algae was during the 1.5 hours of light. The peak near 1 ppm CO_2 indicates that the most sustained hydrogen evolution occurred here.

4.4.3.3 O₂ Yields Decrease with CO₂ Deprivation

Returning to Fig. 2, one sees the decline in O₂ yields with decreasing CO₂ levels. The trend is downward with less carbon dioxide. The algae require CO₂ (*in vivo*) at some level to maintain high rates of electron transport, as indicated by oxygen production. At 0 ppm (pure helium), oxygen activity was 12% of that at 58 ppm. However, an addition of only 0.8 ppm CO₂ (the value where H₂ was maximized) more than doubled the oxygen rate. As expected, oxygen rates did not decline appreciably during the 1.5-h light periods (Fig. 2).

4.4.3.4 Hydrogen to Oxygen Ratios

Only below 10 ppm CO₂ did hydrogen/oxygen-yield ratios approach two (Fig. 5). This observation is in contrast to levels greater than 30 ppm, where the ratio remained less than two. These numbers approximately indicate activity of the hydrogen pathway versus the Calvin cycle. For levels >30 ppm, carbon dioxide assimilation receives the bulk of photoproduced reductant. However, a yield ratio of two or more does not necessarily mean that reductant from PS I and II goes exclusively to the hydrogen pathway because of the presence of transient alternate reductant pools.¹⁸

Fig. 5. Hydrogen: oxygen yield ratios. These ratios (●) are derived from the yields shown in Fig. 3 (1.5 hours of 130 W·m⁻² light). The trend (solid line) is toward ratios of ≥ 2 below 10 ppm CO₂. As explained in the Discussion, the ratios do not necessarily reflect the stoichiometric proportions of water splitting (comparing to the ideal ratio of 2, from Eqn. 1). What one can infer is that, for CO₂ levels greater than 30 ppm, the Calvin cycle overpowers the hydrogen-evolving mode, since hydrogenase manages to wrest only a minor fraction of the reductant from water splitting. This results in a small (<1) H₂/O₂ ratio.

These experiments indicate that atmospheric control of CO₂ concentration is a method of controlling the fate of photosynthetic reductant. In the present case, the amount of carbon dioxide in the algal environment was titrated such that the decreasing CO₂ concentration led to increasing hydrogen yields, with the greatest sustained rate at the 0.8 ppm level. This observation can be explained by a slowing of Calvin cycle activity. With this usual sink for light-generated reductant impaired, the hydrogen pathway (through hydrogenase) can take up an increasing share of electrons. Below 10 ppm CO₂ is where the hydrogen pathway begins to overtake the Calvin cycle, and the yield ratios (H₂/O₂) are ≈ 2 . Conversely, low hydrogen yields (compared to oxygen) combined with short first half-lives (Fig. 4) above 30 ppm CO₂ indicate that the Calvin cycle is the predominant pathway for photogenerated reductant in that region.

On the other hand, carbon dioxide is clearly important for high rates of electron transport (Figs. 2 and 3). Carbon dioxide, or its dissolved form, bicarbonate (HCO₃⁻), acts on the acceptor side of PS II as various investigators have confirmed.^{9,12,13,19} In addition to being the well-known substrate for and activator of the Calvin cycle, carbon dioxide (or HCO₃⁻) helps to assure normal, rapid rates of electron flow through PS II's primary (Q_A) and secondary quinone (Q_B) acceptors, and the plastoquinone (PQ) pool. When the concentration of CO₂ is decreased, reduced efficiency of electron flow occurs, prompting the oxygen-evolving complex to slow its activity accordingly. This "bicarbonate effect" on oxygen-evolving capability by depletion of CO₂ (or HCO₃⁻) has been discussed by Jursinic and Stemler.¹³

In considering the extent to which photosynthetic reductant can be used to produce molecular hydrogen, it is useful to ask the following question: what is the rate-limiting aspect of this process? The limiting step is definitely not the kinetics associated with the chemistry of hydrogen formation, which occurs on a millisecond time scale.²⁰ This can be partially seen in the rapid initial bursts of hydrogen observed in Fig. 2. The limiting step is the generally sluggish movement of electrons generated via photosynthetic water splitting and movement through the electron transport chain.

As discussed above, in a pure helium atmosphere, the rate of electron transport is 12% that at 58 ppm CO₂, whereas only 0.8 ppm CO₂ more than doubles it to 28%. Although hydrogenase is an oxygen-sensitive enzyme, the oxygen evolved in this system is not inhibiting it. Prior experiments have supported this concept by titrating in oxygen upstream from the

algal cell and observing its effect on hydrogenase activity. The photosynthetically produced oxygen is below this threshold.

It is concluded from these experiments that the lower affinity of the Calvin cycle for CO₂ compared to the Photosystem II binding site is the key parameter in determining the extent to which CO₂ assimilation can be bypassed while simultaneously maintaining a fully functional electron transport chain as expressed by photosynthetic oxygen evolution.

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4.5 MILD GASIFICATION PRODUCT CHARACTERIZATION

C. S. Daw, R.L. Graves, A.L. Compere

BACKGROUND

From previous studies it is known that mild gasification of coal produces liquids that are potentially useable as diesel fuel or diesel fuel diluents [1,2]. However, the yield and quality of these liquids as well as the degree of upgrading required can vary substantially with the process severity (i.e., the degree of devolatilization). Char is similar in that the degree of devolatilization directly affects its combustion properties. The economic viability of any mild-gasification process is thus determined by tradeoffs among product yield, upgrading costs, and end-use requirements.

PROJECT DESCRIPTION

The purpose of this investigation is to develop basic characterization data for the liquid and char products of mild gasification. Such data are needed to evaluate key relationships among process conditions, product yield, and product end-use value. Of particular interest is the suitability of the liquid (with minimal upgrading) as diesel fuel and the suitability of the char as boiler fuel, although non-fuel uses of these products are also considered.

Representative samples of mild-gasification liquids and chars are being obtained from industrial groups involved in the development of candidate processes. These samples are subjected to a variety of characterization tests including:

- chemical and physical analyses of the char and liquids;
- combustion testing of the liquids in a diesel engine; and
- combustion testing of the chars in laboratory reactors.

In general, ORNL is tasked to carry out the more detailed, unconventional laboratory characterizations such as proton NMR (nuclear magnetic resonance), FTIR (Fourier transform infra-red) spectroscopy, and neutron activation. Standard laboratory assays are carried out either by ORNL or major mild gasification teams. The use of the liquids as engine fuels, with either blending or mild upgrading, is still of interest so those evaluations have been continued. Although there are several high-value products that can be derived

from the char, its use as fuel remains a potentially large market. In addition, it is anticipated that char combustion will supply a major fraction of process heat in commercial mild-gasification processes. Hence a basic understanding of the char combustion properties is important.

DISCUSSION OF CURRENT ACTIVITIES

Exploratory work to derive as much usable fuel material from mild gasification liquids continued in October 1992 at a modest level of effort. Coal liquid middle distillate aromatics are normally removed to decrease ignition delay and improve fuel performance toward that of conventional diesel fuel. The WRI liquids that were caustic washed last year produced viable diesel fuel extenders. The aromatic fraction that was removed in the caustic wash was retained and used to produce derivative fuel materials. Ignition delay of a mixture of the prepared derivative and diesel fuel was measured this month in an engine test. Although we only used 10% of the material in diesel fuel, there was no apparent performance degradation. The only problem was the high viscosity of the material itself. It may be possible to control viscosity by optimizing chain length of the derivatives. This test is important for two reasons: 1) it significantly improves fuel production from a given amount of coal by permitting use of the aromatic fraction of middle distillate coal liquid s, currently removed by caustic washing, in effective diesel fuels and 2) the derivatives appear to have better engine performance than caustic washed coal middle distillates. Being able to effectively use the 40% aromatics removed by caustic washing could be a deciding factor in commercial viability of coal liquid production.

A sample of coal liquid distillate received from the University of North Dakota Energy and Environmental Research Center was blended in equal volume proportions with Phillips No. 2 Diesel fuel and engine tested. The feed coal was Indiana #3, and the raw liquid was distilled at 215-382°C. The density of the distillate as-received was 0.996 g/cc at 20°C, quite heavy compared to the typical 0.850 g/cc for diesel fuel. Given the small volume of distillate available, it was not caustic washed. Although the fuel blend performed relatively well, a small amount of tar-like precipitate formed on blending with the diesel fuel. Measurement of the ignition delay of the fuel blend indicated an apparent cetane number on the order of 28-30 (cetane number of typical No. 2 diesel fuel is 45). A small sample will be retained for

further analysis (e.g., simulated distillation, elemental analysis), and the remainder will be blended with diesel fuel in a different proportion and engine tested.

The principal effort for FY 1993 will be to characterize products from the SGI process. A pilot plant is being operated with the SGI process by Maumee Research in Ohio. Maumee Research has been contacted regarding shipping of samples of coals and coproducts to ORNL for analysis. A full set of samples from the baseline coal and a lignite are ready to be sent to ORNL.

The final report for FY 1992 work with Babcock and Wilcox (B&W) under the Cooperative Research and Development Agreement (CRADA) ORNL-91-0066, "Characterization and Modeling Combustion of Mild-Gasification Chars in Pressurized Fluidized Beds," was completed and was transmitted to METC.

5. COAL COMBUSTION RESEARCH

R. L. Graves

5.1 ANALYSIS OF FBC DETERMINISTIC CHAOS

C.S. Daw

DISCUSSION OF CURRENT ACTIVITIES

Activity during this reporting period was focused on analysis of fluidized bed data and development of improved analysis algorithms. Experiments likely to demonstrate the onset of chaos in fluidized beds as well as the potential control of chaos were also defined.

Fluidized Beds

Experimental measurement of voidage and pressure signals from fluidized beds at the University of Tennessee, Morgantown Energy Technology Center, Foster Wheeler Development Corporation, and Babcock and Wilcox Alliance Research Center have continued. Measurements from the University of Tennessee and Morgantown have involved operating parameter variations of sufficient detail to allow clear observations of flow transitions and the correspondence of specific physical phenomena with features in phase space. It has also been possible to directly compare typical fluidization patterns of solids from three different characteristic (Geldart) groups, B, D, and A. From these comparisons it appears that entropy is a good overall index for distinguishing between characteristic fluidization regimes, while detailed phase space structure is more useful for highlighting subtle differences within a regime.

It is expected that both entropy and phase space structure can be used directly as process state indicators for developing improved fluidization control strategies. One strategy of particular interest currently is an adaptation of the so-called OGY method developed specifically for chaotic systems (1). This method is of particular interest because it can be used to completely eliminate or, conversely, enhance the level of chaos without changing the nominal values of the operating parameters. We are now working with collaborators at the

University of Tennessee and Morgantown Energy Technology Center to construct experiments that can demonstrate this method in fluidized beds. Two different experimental designs have been selected, one focusing on slugging operation and one on bubbling. In both cases the basic approach is to adapt the OGY method for controlling the formation of slugs and individual bubbles, respectively.

Another simpler control method which is based on the time-average phase-space structure has already been experimentally demonstrated for application to fluidized bed contactors in the Y-12 Plant. A patent application entitled "Fluidization Quality Analyzer and Automatic Control Loop for Fluidized Beds" (No. 07/964,830) was submitted on this method last October.

Collaboration with other groups involved in fluidized bed data analysis through the Electric Power Research Institute has led to still further improvement in the algorithms for estimating entropy and correlation dimension. In particular, statistical methods originating with Floris Takens at the University of Groningen in The Netherlands have been successfully incorporated to yield even more efficient algorithms.

Two papers on fluidized bed applications were presented at the AIChE National Meeting in November 1992 (2&3). The first of these (2) has been submitted and accepted for publication in the AIChE Symposium Series. Two other papers (4&5) have been accepted for presentation and publication at the International Fluidized Bed Combustion Conference in May 1993. Another paper (6) has been submitted for presentation at the next AIChE National Meeting.

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5.2 TECHNICAL SUPPORT TO PETC-USAID COLLABORATIVE COAL PROJECTS

R. P. Krishnan

BACKGROUND

In response to the request from the Pittsburgh Energy Technical Center (PETC), the Oak Ridge National Laboratory (ORNL) is providing technical assistance in the implementation of collaborative coal projects under the U.S. Agency for International Development (USAID)/Government of India (GOI) Phase II, Alternative Energy Resources Development (AERD) Project.

In May 1983, the GOI and the USAID initiated the AERD project with a coal conversion component comprising of six collaborative coal projects.

- (1) Evaluation of freeboard performance in a fluidized bed combustor (FBC)
- (2) Scale-up of an atmospheric fluidized bed combustion boiler
- (3) Rheology, stability, and combustion of coal-water slurries
- (4) Beneficiation of fine coals in dense media cyclones
- (5) Hot gas cleanup and separation
- (6) Cold gas cleanup and separation

The PETC, USDOE under a Participation Agency Service Agreement (PASA) had the management responsibility for implementing the collaborative coal projects. In the FBC projects, ORNL and BHEL, Trichy, India, were designated as the lead institutions for the collaborative efforts.

The successful completion of the above coal projects in June 1987 led to a strong interest by the participants in the AERD coal conversion projects to continue the involvement of USAID and the USDOE/PETC in the following coal projects under the AERD, Phase 2 coal conversion activities.

Project 1

Development of Pollution Control Strategies for Abatement of NO_x and SO₂ Emissions from Coal-Fired Power Plants

Nitrogen and sulfur oxide emissions from fossil-fired power plants are expected to increase significantly with the installation of additional coal-fired power plants in India. The composition and characteristics of Indian coals are different from U.S. coals and this will impact the selection of pollution control strategy. The existing data base in India on NO_x/SO₂ emissions from coal-fired power plants is not adequate to quantitatively define the magnitude of the emissions, which is the first step in the evaluation of control options.

The objectives of this project are to establish the necessary data base on NO_x/SO₂ emissions by (1) baseline monitoring in selected power plants in India using the state-of-the-art techniques developed in the U.S.; (2) testing known in-furnace control strategies practiced in the U.S. in selected power plants, in India (3) bench-and pilot-scale testing of Indian coals to quantify NO_x/SO₂ emissions; and (4) simulation and modeling of the combustion and heat-transfer processes in the boiler for NO_x/SO₂ prediction.

The BHEL, Trichy, will carry out the projects in India as part of their ongoing research and development on NO_x/SO₂ control from coal-fired power plants. Technical assistance from the U.S. will include identification and procurement of state-of-the-art equipment for NO_x/SO₂ measurement, and training of the BHEL engineers in selected U.S. utilities (TVA and others) on NO_x/SO₂ monitoring and control technologies, and participation of U.S. experts in the existing bench-scale/pilot-scale testing activities at BHEL and in the baseline monitoring of Indian power plants.

Project 2

Slagging Combustor Development for High-Ash Indian Coals

Indian coals have ash content in the range of 35 to 50% and ash fusion temperature over 1482° C (2700° F). For coals of such high-ash content, it would be advantageous from the operational, reliability, and boiler life considerations if the ash can be successfully rejected as a molten slag rather than be allowed to carry over with the flue gas as in conventional pulverized fuel boilers. The slagging coal combustor (SCC) has been developed along these lines and is now in the demonstration stage in the United States.

Recognizing the potential for this technology in India, the BHEL has an active research and development program under way. A 3.0 MW(t) process development unit has been erected and is in operation at Trichy. However, there are several fundamental and engineering issues that are yet to be resolved with respect to Indian coals (slagging potential, slag rejection -- quantity and slag properties, ash carry-over from the combustor, optimum air preheat system, operating flexibility -- start-up, shut-down, and effect of design parameters on slag recovery and combustor operation, carbon utilization and NO_x/SO_2 emissions) before the slagging combustor can be recommended for commercial applications.

The objectives of this project are to (1) demonstrate whether the slagging combustor technology is suited for Indian coals, (2) identify the engineering problems associated with the design, operation and scale-up of the combustor, and (3) design modifications needed in the BHEL slagging combustor to conduct long duration test runs on a variety of Indian coals differing in ash content and slagging tendency.

U.S. technical assistance in the design review of the BHEL slagging combustor, screening and selection of Indian coals based on their slagging potential, and on-site participation in the testing and data analysis is envisaged.

Project 3

Characterization of Indian Coals for Combustion and Gasification

With the deteriorating quality of coal in India (highly erosive coal) coupled with fuel switching by utilities, there is a critical need to quantify the impact of coal quality on power plant performance. Pilot-scale combustion tests are mandatory to provide boiler performance data on combustion efficiency, fuel ignition characteristics, flame stabilization, slagging, fouling, erosion and corrosion of boiler components, and gaseous and particulate emissions. Pilot-scale tests are also necessary for the full-scale burning in commercial boilers. In India, there is no facility available to conduct screening tests on coal.

The objective of this project is to design, erect and commission a pilot-scale Fuels Evaluation Test Facility (FETF) at BHEL, Trichy, which will serve as a focal point for combustion research in India. The PETC combustion research division and the ORNL will be the lead U.S. institutions collaborating with BHEL, Trichy in this project.

Project 4

Residual Life Assessment and Life Extension of Coal-Fired Power Plants

The assessment of remaining life of coal-fired power plant components based on quantitative, nondestructive, real-time measurements of the extent of damage to these components is an area which is actively pursued in most advanced countries where the latest diagnostic tools are available. The methodologies and techniques are the key to a successful remaining life assessment program. In keeping with the need for steady and reliable electric supply, the Ministry of Power, Government of India has recently embarked on a multi-million dollar power plant life assessment and rehabilitation program.

This project will be a collaborative effort, initially between the BHEL and the Electric Power Research Institute (EPRI), in which the diagnostic techniques, design criteria, methodologies, and implementation strategies developed by EPRI for the U.S. utilities will be tested in selected Indian utilities. The highly erosive nature of Indian coals will provide an opportunity to test the engineering correlations for prediction of erosion of boiler and auxiliary components, and possibly extended their range of applicability.

Project 5

Environmental and Natural Resource Analysis of Coal Cycle

The mining, conversion, and disposal of waste and byproducts from coal utilization have serious environmental repercussions in India. Although there are regulations stipulated for air and water quality pollutants, they are not strictly enforced except in urban areas. This policy is going to change in the near future, and several groups are working in the country on allowable limits, environmental considerations for power plant siting, and impact of air/water/soil quality in the vicinity of coal mines and coal burning facilities. In all these tasks, environmental system models and an environmental data base are vital. Air and water quality data are only now being collected in India, mainly around the large power plants in central India.

The goal of this project is to develop environmental system models for prediction of air and water quality near coal-based power plants. The present data base will only permit development of the overall structure of the model and the process/environmental data needed as inputs for the system model. It is expected that the model can be refined as more data

becomes available. The methodology and the model inputs and outputs will be established in this project.

The project will be carried out by the Tata Energy Research Institute (TERI), New Delhi. Assistance to TERI will be provided by ORNL, PETC, EPA in the screening, selection and adaption of the air/water quality prediction models developed in the U.S. for local conditions.

DISCUSSIONS OF CURRENT ACTIVITIES

Fuels Evaluation Test Facility

The AERD grant agreement between USAID and GOI ended on June 30, 1992, after ten years which is typically the maximum permissible duration for a USAID project grant agreement. At this time, four out of the five coal projects which were initiated under AERD, Phase 2 were essentially completed. The accomplishments in the completed projects (Projects 1, 2, 4, and 5) were reported in the previous Semi-Annual Report (April 92 - September 92).

The Fuels Evaluation Test Facility (FETF) (Project 3) was also scheduled for completion in June 1992. However, due to unforeseen international events that occurred in 1991 (the foreign exchange crunch faced by India and the Middle East Crisis the project could not be completed in June 1992, as planned. PETC and ORNL at the request of USAID has continued to provide technical assistance to BHEL. The facility is now slated for completion in July 1993, and will be ready for early shakedown testing in late summer.

R. P. Krishnan visited the test site in March 1993, to witness the erection of the FETF and to plan with BHEL the commissioning and shakedown activities.

The FETF being set up at Trichy, is a versatile fuels test facility and is thermally rated at 3.0 million BTU/h. It will be the first such facility in South East Asia. The total project expenditure to date is roughly US \$2.5 million. USAID contribution is US \$1.0 million. The FETF will enhance the capability of BHEL to understand and solve fuel related problems in their existing commercial boilers as well as conduct prior evaluation on fuels and fuel blends to incorporate in the utility boilers appropriate systems for combustion, heat absorption, and pollutant abatement at the design stage itself. Testing fuels in the FETF will be cheaper, quicker and more flexible than testing in a commercial boiler.

A schematic of the FETF is shown in Figure 1. The furnace, convection and the coal/ash handling system and the structural support for these components add up to roughly 120 tons of steel. Nearly 70% of the erection work has been completed. Erection of the main furnace of assembly (Figure 2) consisting of five individual refractory-lined blocks is expected to be completed in mid-May 1993. The erection of convection section will follow once the furnace is installed. The remaining work on the furnace itself will include external insulation, installation of the heat exchangers in the convection pass, mounting the slagging and fouling panels, the burner assembly and the cooling water system. Fabrication of the wall burners and the corner burners is in progress and will be ready when the furnace is erected.

Engineering design and fabrication of the soot blowers, orifice meters and fouling/slagging probes is in progress but these will not be needed until the first commissioning phase of the FETF is completed.

The flooring and plastering work in the control room was in progress during the visit. The motor control center has been installed and commissioned. Utility connections will be provided once the erection of furnace and convection pass is completed. The instrumentation and control panel has been ordered and is expected to be delivered by end of April 1993. All of the USAID supplied equipment has reached the site. They are still to be tested which will start after the furnace erection is completed. Technical assistance from PETC and ORNL during this initial period is anticipated. USAID, New Delhi, is aware of the need for continuation of on-site technical assistance and additional funding for this project. A decision is awaited. In the interim period, ORNL and PETC will continue to provide necessary assistance to BHEL through correspondence.

Demonstration Project on Coal-Fired Power Plant Condition Assessment and Remaining Life Assessment in India

The demonstration project is part of the recently approved USAID/Government of India (GOI) Energy Management Consultancy and Training (EM CAT) project. Under EMCAT, USAID has provided a US \$14.0 million grant assistance to the Power Finance Corporation (PFC), a newly formed autonomous financial institution of the Department of Power, GOI. PFC provides funds to the various state and federal utilities in India for new power projects as well as renovation, modernization and environmental upgradation of

existing plants. One of the criteria imposed on the utilities seeking funds from PFC is to perform and prepare a plant life condition assessment document clearly delineating the benefits that will accrue the utility by refurbishing/upgrading the existing plant. However, the utilities in India are lacking the tools and the technical skills to conduct such an assessment.

The demonstration project will be one of the activities to be covered under the USAID/GOI EMCAT agreement. ORNL will provide technical assistance and cross-out technical coordination in the implementation of the demonstration project. The PETC, similar to the AERD agreement, under a Participating Agency Service Agreement (PASA) with USAID, New Delhi, will manage the project. Technical support and training of Indian utility engineers in plant life assessment techniques will be provided by the Tennessee Valley Authority (TVA), Electric Power Research Institute (EPRI), and US engineering and consulting companies engaged in coal-fired power plant condition assessment.

The demonstration activities will include:

1. Review plant records to assess present plant condition in terms of plant operation and heat rate, plant availability and load factor, forced outage and failure modes, maintenance practices, environmental compliance, overall plant management, and utility staff. These data will establish the "present" plant condition and the "starting" point for the follow-on condition assessment activities. The type of inspections and examinations to be conducted, the procedures, and the sequence of examination by major component areas will be identified and documented.
2. Assess current condition and remaining life of all major critical components and equipment (boiler, turbine, generator, coal/ash handling systems, piping, fans, pulverizers, electrical system, condensers and water treatment system) by visual inspection, non-destructive techniques, sample analysis, etc. under the guidance of U.S. experts and per the codes and procedures adopted by U.S. utilities after discussions with the concerned utility.

3. Analyze and interpret field data by joint U.S. and Indian expert teams to identify the causes of failure and suggest corrective measures to prevent failures, extend component life, and increase plant availability/efficiency with accompanying cost/benefit analysis in consultation with PFC and the SEB. Corrective measures will be discussed with the utility and PFC before finalization.
4. Documentation of the methodologies and procedures used in the condition assessment, the results and the recommendations with respect to replacement and/or repair and plant maintenance/operation in a final project report which can form the basis for investment and analysis by Indian utilities and the PFC.
5. Train Indian engineers, utilities and project management staff, etc. in the U.S. and India before, during, and after the project; establish a training program in India based on the demonstration project for future training of engineers in specific areas of coal-fired power plant life assessment.

R. P. Krishnan met with PFC during March 8-12, 1993, in New Delhi, to discuss the implementation strategy and the work plan for this new activity under PETC. PFC indicated that the BHEL, and National Thermal Power Corporation -- a federal utility, will be the lead agencies in India that will conduct the demonstration with the US team. The utility site will be finalized by PFC in May 1993, and communicated to PETC.

During the next reporting period, the progress on the FETF and the activities in the recently initiated USAID/PETC power plant life assessment project will be covered.

6. FOSSIL FUELS SUPPLIES MODELING AND RESEARCH

6.1 STRATEGIC PETROLEUM RESERVE PLANNING AND MODELING

P. N. Leiby

INTRODUCTION

The Strategic Petroleum Reserve (SPR) is a government-owned stockpile of crude oil intended to serve as a buffer against possible oil market disruptions. The overall purpose of this project is to develop and apply improved models for SPR long-run planning. Current project efforts emphasize developing new ways to explicitly and flexibly portray this uncertainty or risk.

DISCUSSION OF CURRENT ACTIVITIES

Recent efforts have completed a risk-based SPR planning model (called SPR-Risk). The motivation for the SPR-Risk model is to provide a simple summary of the SPR behavior and results obtained from some of the larger SPR models (DISSPR, ORNLTEIS, and Hogan-Leiby), embedded in a framework which highlights risk and uncertainty. The SPR-Risk model is a PC-based, interactive, and user-friendly system. The SPR-Risk model is basically a spreadsheet connected to a risk-analysis engine (@Risk), with a smooth front-end for user control and output. It is executable under modifiable assumptions by a general audience of DOE managers. A variety of SPR planning questions are closely related to the anticipated frequency and rate of SPR drawdowns. Planning may also benefit from considering SPR outcomes in a framework which displays risk and the range of possible outcomes.

The completed version of the SPR-Risk model which enhances the analyses previously performed with the DOE's DISSPR model is called DIS-Risk. It is currently being exercised

for planning experiments, and has been documented in "DIS-Risk Model for SPR Analysis: Model Documentation and Benchmarking Results".

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