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FOSSIL ENERGY PROGRAM SEMIANNUAL PROGRESS REPORT
FOR OCTOBER 1991 THROUGH MARCH 1992

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Program Manager

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- ORNL-6634 Fossil Energy Program Semiannual Progress Report for October 1989 Through March 1990
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FOSSIL ENERGY PROGRAM SEMIANNUAL PROGRESS REPORT FOR OCTOBER 1991 THROUGH MARCH 1992¹

R. R. Judkins, Program Manager

ABSTRACT

This report covers progress made during the period October 1, 1991, through March 31, 1992, 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 Office of Basic Energy Sciences, the DOE Fossil Energy Office of Petroleum Reserves, the DOE Fossil Energy Naval Petroleum and Oil Shale Reserves, and the U.S. Agency for International Development. The Fossil Energy Program organization chart is shown in the appendix.

1. SUMMARY

1.1 MATERIALS RESEARCH AND DEVELOPMENT

The materials research and development for fossil energy applications at Oak Ridge National Laboratory consists of: ceramics development for high temperature applications, new metal alloys with unique mechanical properties, and corrosion research to understand the material behavior in combustion and conversion environments. The transfer of technology funded under this program is enhanced with concerted efforts to interact with industry, perform joint programs, and work with those interested in using the technology.

Emphasis this period was on various methods of fabricating ceramic composite tubing by CVID infiltration of several preforms containing chopped fibers, ceramic membranes for

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hydrogen separation, and the role that ionic and electronic conductivity play in the microwave sintering of lanthanum chromite for fuel cells. Alloy development of iron aluminides continues with creep testing, weldability, environmental effects and fracture behavior. Studies on a lower aluminum version of these alloys are showing promise for immediate technical transfer applications. Austenitic alloys were pursued for advanced heat recovery and hot gas cleanup, and fundamental studies on corrosion continued. Our materials technical support to the Wilsonville (Alabama) Advanced Coal Liquefaction Facility, the Great Plains Coal Gasification Plant and selected Clean Coal Technology Program Projects continued.

SiC has progressed to be a viable candidate for fossil systems applications, and a primary need is for high temperature heat exchangers. Composite tubing for increased fracture toughness is under development. The forced chemical vapor infiltration and deposition (FCVID) method invented at ORNL, incorporating a temperature gradient, shows the most promise for thicker wall tubing. A variety of preforms and filler materials to build up the wall, reduce costs, and densify the tubing have been used. A technique that appears to have much promise uses a loosely wound preform filled with chopped fibers prior to FCVID processing. It also increases the potential for cost savings by reducing the amount of the comparatively expensive Nicalon® needed. Machining and characterizing of tubing produced in this manner are underway.

Activities have increased to expedite the declassification and technology transfer of ceramic membranes that have promise for separating hydrogen from coal-derived gases at high temperatures.

Lanthanum chromite is often the design material for fuel cells that acts as the electrical interconnect between the stacks of electrolytic cells. A composition of lanthanum chromite was microwave sintered and annealed and the special microwave effect did not occur with this material as it did with alumina and zirconia. An investigation is continuing to understand the role that ionic and electronic conductivity play in determining the microwave coupling of materials.

The evaluation of some of the advanced austenitic alloys, such as the lean stainless steels and modified alloy 800, are being completed and discussions with industry on applications for their use are underway. Long-time creep testing of the lean stainless steels have now exceeded 50,000 h at 700°C and continue to show excellent strength and ductility.

Studies of the addition of nitrogen indicate that strengthening may occur without the need to cold or warm work the alloys to develop strengthening mechanisms. A modified alloy 800H that has been cold finished, solution treated at 1190°C and cold pilgered has twice the strength of alloy 800H at temperatures to 760°C. Testing times are still short so long term stability is yet unknown. RA333 and Haynes alloy 556 have been examined for use in the Tidd hot-gas clean-up vessel and highly alloyed, nickel-chromium materials are being examined.

In supporting several fossil energy facilities, the staff of a coal gasification plant was assisted in identifying a means to eliminate corrosion in a distillation column. Specimens were provided to the Mitsui SRC Development Company, Ltd. for exposure in their coal liquefaction facility and specimens provided by Mitsui were exposed in two reactor vessels at the Wilsonville Coal Liquefaction Research and Development Facility. A review was conducted of the materials selected for the fans and heat exchangers of the Selective Catalytic Reduction project to be located at Gulf Power Company's Crist Unit 5. Since the Wilsonville (Alabama) Advanced Coal Liquefaction Facility has been closed, arrangements were made to retrieve all ORNL-supplied samples and to examine selected components.

Research on Fe_3Al alloys has shown that specific compositions coupled with thermomechanical processing techniques can produce room temperature ductilities of 10-20% and yield strengths of 500 Mpa up to 600°C. The creep resistance can also be increased with small additions of Mo, Nb, and Zr. The properties of commercially melted large heats of FA-129 have been examined. Microalloying to produce improved creep resistance and yet retain weldability is being pursued. Analytical electron microscopy has been performed to identify precipitates and correlate precipitate compositions with properties.

Several iron aluminide compositions are being evaluated in atmospheres typical of coal gasifiers involving gases with relatively low oxygen and high sulfur activities. Specimens of FeCrAl were compared with Fe_3Al alloys containing chromium after exposure to gas mixtures of H_2S - H_2 - H_2O at 700 to 800°C. Again, the higher aluminum increases sulfidation resistance even in FeCrAl alloys when large amounts of chromium are also present. When tested in the sulfidizing atmospheres, the alloys containing 2 at.% Mo and 0 and 4 at.% Cr indicated significantly reduced corrosion rates when compared with chromium containing alloys with no molybdenum. Thus, Mo appears to suppress the adverse effect of Cr

additions. Aqueous corrosion studies have shown that the addition of 1 to 2 at.% Mo significantly increases the resistance of Fe₃Al alloys to attack in acid chloride solutions.

The effect of aluminum on ductility, environmental embrittlement, creep, oxidation and sulfidation resistance is being examined. A family of lower aluminum alloys has been found to have more immediate technology transfer potential.

1.2 ENVIRONMENTAL ANALYSIS SUPPORT

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 Program. A key activity was the preparation for PETC of a preliminary 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 Program. Assistance also was provided to the DOE Office of Fossil Energy in evaluating the environmental aspects of projects proposed for cost-shared funding under the fourth round of the Clean Coal Program.

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. Activities are also continuing on the study of mild gasification of coal.

1.4 COAL COMBUSTION RESEARCH

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.

1.5 FOSSIL FUEL SUPPLIES MODELING AND RESEARCH

Project work focused on the benefits of increasing the drawdown and distribution capability of the Strategic Petroleum Reserve (SPR). In a study by Trumble and Lee (1991), two models (DISSPR and ORNLTEIS) were used to compute the expected benefits of alternative drawdown and distribution capabilities. The analysis took into account the probabilities of oil supply disruptions, the availability of other sources of supply to offset the disruption, the elasticities of oil demand, and other market parameters. If we assume a one-billion barrel reserve and disruption times of six months or longer, then expanding the sustained drawdown and distribution capability beyond 5.5 million barrels per day is unwarranted, simply because the reserve would be exhausted in six months at that rate. Conclusions regarding the value of drawdown rate expansion thus depend strongly on assumptions regarding the expected length of disruptions, and on the likelihood of multiple, large disruptions in succession.

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 on iron aluminides, development and evaluation of advanced austenitic alloys, evaluation of materials for hot-gas filter support systems, fundamental studies of erosion and corrosion, and materials testing and failure analysis support to coal conversion and utilization plants.

2.1 FIBER-REINFORCED TUBULAR COMPOSITES BY CHEMICAL VAPOR INFILTRATION

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

INTRODUCTION

A forced-flow thermal-gradient chemical vapor infiltration process has been developed to fabricate composites of thick-walled tubular geometry common to many components. Fibrous preforms of different fiber architectures (3-dimensionally braided and filament wound) have been investigated to accommodate components with different mechanical property requirements. This paper will discuss the fabrication of tubular, fiber-reinforced SiC matrix composites and their mechanical properties.

Fiber-reinforced SiC-matrix composites appear promising for gas turbine applications because of their high strength at elevated temperature, light weight, thermal shock resistance, damage tolerance, and oxidation and corrosion resistance. However, incorporation of continuous ceramic fibers into ceramic matrices without significant damage to the fibers is difficult. Hot-pressing of fiber-reinforced composites is impractical because the extremes of temperature and pressure weaken the continuous fibers. Cold-pressing and sintering routes to the fabrication of composites are of no value because typical sintering temperatures greatly exceed the temperature limit of the fibers.^{1,2} Because of these limitations several novel impregnation processes have been developed. One such process impregnates a fibrous preform with liquid precursors that transform to ceramic materials on heat treating.³⁻⁵ A second process impregnates a fibrous preform with extremely fine metallic silicon which converts to silicon nitride when reacted with nitrogen gas at elevated temperatures.^{6,7} The greatest success has been achieved by vapor-phase processing, leading to a class of techniques termed chemical vapor infiltration (CVI). Two distinctly different vapor phase processes have been used to fabricate matrices: isothermal CVI,⁸⁻¹¹ which is used commercially, and forced CVI under development at Oak Ridge National Laboratory (ORNL).¹²⁻¹⁵

Fiber-reinforced composites are being considered for combustors, burner tubes, heat exchangers, headers, hot-gas filters and even rotors for stationary gas turbine engines. Unfortunately, neither of the CVI processes described above has demonstrated the ability to fabricate thick-walled tubular shapes appropriate for turbine engines. Isothermal CVI is

ideal for the fabrication of thin-walled structures including complex shapes, however, infiltration times become extremely long for thick cross sections. The forced CVI process has been developed for thick-wall plates, however, very few tubular shapes have been infiltrated. Therefore, the focus of this investigation was the development of the forced CVI process for the fabrication of thick-walled tubular composites.

Fibrous Preforms

Nicalon fiber preforms of a tubular geometry (2.5 to 3.8 cm ID; 0.6 cm wall thickness; ~15 cm long) were fabricated with different fiber architectures. Nicalon is a polymer derived SiC fiber that is microcrystalline or amorphous in nature and contains significant amounts of silica.^{16,17} Filament winding of fiber tows was used to fabricate components that require high hoop or radial strengths, but relatively modest axial strengths. A fiber architecture of this type would be ideal for combustors or headers. Three dimensional braiding was used to fabricate components for applications such as burner tubes or heat exchangers that require high axial strengths but only modest hoop strengths. Preforms were also fabricated by wrapping layers of cloth around a mandrel so that half the fibers were in the hoop direction and half in the axial direction. Filament wound preforms formed on graphite mandrels were prepared by the K-25 plant in Oak Ridge. The graphite mandrels contained hundreds of holes to permit ready access of reactant gases to the fibrous preform. The initial preforms were unidirectionally wound with the fibers less than 1° off the hoop direction. Satisfactory tubes with fiber contents of 45 to 55 vol % were produced, but because of the small angle, expected strengths in the axial direction are minimal. Therefore, tubes were produced with the fibers 10° off the hoop direction to increase the axial strength (Fig. 1). Initially, space was left between fiber tows, however, large pores became aligned on top of each other making thorough infiltration difficult. The winding technique was then modified to place adjacent tows in contact. This winding technique produced a density of about 47 vol % and prevented the formation of large pores in the preform.

Quadrax Corporation* prepared 3D braided preforms on graphite mandrels for this study. The initial tubes were braided very loosely and contained only about 15 vol% Nicalon fibers (Fig. 1). Near the ends of the preforms, the braided fibers were bound to the mandrel with graphite yarn to prevent the braid from unraveling. Infiltration of such a low density

*Quadrax Corporation - 300 High Point Avenue, Portsmouth, R.I.

preform proved to be impossible with the forced CVI process. Therefore, researchers at Quadrax Corporation modified their process in order to fabricate tubes containing up to 40 vol % Nicalon fibers.

ORNL-PHOTO 91-4383

DIFFERENT FIBER ARCHITECTURES ARE BEING INVESTIGATED

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Fig. 1. Preforms with different fiber architectures; (left) filament wound with fibers 10° off the hoop direction, (center) same except adjacent tows are touching, (right) 3-D braid.

In another approach, a process was developed to fabricate preforms for hot-gas filters that combines continuous and chopped fibers. The continuous fiber produces the strength, damage tolerance, and thermal shock resistance while the chopped fibers control the permeability and filtering efficiency of the filter surface. Preforms of this type are fabricated by fiber molding chopped fibers into the open pores of a braided substrate. Hybrid preforms have proven to be ideal for hot gas filter applications in work being performed at The 3M Company. One further advantage of the process is that expensive Nicalon fibers can be replaced by less expensive chopped alumina or Nextel fibers. Because of the reduced cost, hybrid preforms may also find application in heat exchangers or regenerators where strength requirements are quite modest.

Fiber-Matrix Interface

The mechanical properties of fiber-reinforced ceramic composites are controlled by the amount of fiber in each orientation and the strength of the bond between the fibers and the matrix.¹⁸ Experience has shown brittle composites result when the SiC matrix is applied directly onto the Nicalon fibers. Fracture surfaces for these materials are flat and smooth with no evidence of fiber pullout that results in toughening. To control the interfacial bond strength and protect the fibers from the corrosive, HCl laden CVI atmosphere, a thin layer of pyrolytic carbon (0.1 to 0.5 μm thick) is deposited onto the Nicalon fibers. The lamellar structure of the graphitic carbon coating protects the fibers from HCl attack and promotes the movement or slip of the fiber within the matrix.

CVI Processing

Forced chemical vapor infiltration as developed at the Oak Ridge National Laboratory utilizes a thermal gradient and a pressure gradient to efficiently infiltrate simple flat plate preforms of thick cross-section. The forced CVI process was recently modified so that tubular preforms could be infiltrated by creating a thermal gradient from the outside of the tube to the inside.¹⁹ While the outside of the preform is heated, cold water is circulated through the stainless steel injector in order to cool the inside diameter of the fibrous preform (Fig. 2). The gaseous reactants enter the furnace through tubing that runs within the water cooling passage. Reactants flow from the tubing in the cooling passage into a graphite gas distributor and are dispersed along the length of the preform through parallel slots in this distributor. Reactants then proceed uniformly through holes in the graphite mandrel into the preform (Fig. 3).

Densification of the tubular preforms occurs when hydrogen and methyltrichlorosilane (CH_3SiCl_3 or MTS) flow through the mandrel. Decomposition of the MTS and deposition of SiC occurs as the gases approach the higher temperature regions near the outer diameter of the preform. Deposition of SiC within the hot region of the preform increases the density and thermal conductivity of the material. Therefore, the deposition zone moves from the outer diameter, hotter regions toward the inner diameter, cooler regions.

Filament wound preforms were effectively infiltrated from the outset using this system. The high fiber content of the preform produced a sufficient backpressure to disperse the reactants along the length of the tube allowing them to flow uniformly through the walls

ORNL-PHOTO 4382-91

WATER COOLED GAS DISTRIBUTOR MAINTAINS THERMAL GRADIENT DURING INFILTRATION

ORNL-DWG 91-9920

FORCED CVI PROCESS FOR INFILTRATING TUBULAR COMPOSITES

Fig. 2. Schematic of equipment distributor used to infiltrate tubular preforms.

Fig. 3. Photo of graphite gas distributor and mandrel for infiltrating tubular composites.

of the preform. The microstructure of filament wound composites (Fig. 4a) demonstrates that the limited amount of porosity is distributed uniformly through the thickness. In contrast, flat plate preforms produced by cloth layups result in a very different microstructure (Fig. 4b). Flat plate preforms contain greater amounts of porosity and have a tendency for voids to line up regardless of the layup (0° - 90° vs 30° - 60° - 90° etc.).

ORNL-PHOTO 4384-91

FILAMENT WOUND TUBULAR PREFORMS HAVE BEEN INFILTRATED

C-RING STRENGTH - 840 MPa

Fig. 4a. Microstructure of filament wound tubular composite.

Braided preforms were much more difficult to infiltrate than filament wound preforms. Braided preforms with a fiber content of only 15 vol% were investigated initially. The low fiber content and large gaps between fiber bundles created voids that extended through the thickness of the preform. Because of these voids, no backpressure was created by the preform to disperse reactants along the length of the tube. Therefore, reactant gases entered the center of the preform and flowed directly through the walls so that very little SiC was deposited. Preforms that had been braided to a fiber loading of 33 vol % were also infiltrated. The porosity created by this braid was more uniformly distributed, however the permeability was relatively high and reactants moved through the preform so that little deposition occurred near the ends of the preform. Braided preforms with still higher

ORNL-PHOTO 2399-85

COMPOSITES WITH DENSITIES EXCEEDING 80% HAVE BEEN PRODUCED BY INFILTRATING CLOTH-REINFORCED PREFORMS

Fig. 4b. Microstructure of a flat plate type composite (cloth layup preform). Note the interconnected porosity from layer to layer in the flat plate composite.

densities will be required to obtain proper infiltration. Preforms fabricated for use as hot-gas filters containing braided continuous fibers and fiber molded chopped fibers were also investigated. Since chopped fibers are much less permeable to gases than cloth, the hybrid preform created a significant backpressure that dispersed the reactants along the length of the tubular preform. The uniform movement of reactants through the preform resulted in SiC being deposited in the hot outer region of the tube. After sufficient densification occurred, the infiltration proceeded to the center and inner diameter of the preform.

Mechanical Properties

The mechanical properties of SiC matrix composites reinforced with Nicalon fibers have been characterized when fabricated as simple disks.¹⁹ Forced CVI composites exhibit an average flexure strength of ~380 MPa and an apparent fracture toughness of ~23 MPa·m^{1/2}. To date, the mechanical property characterization of tubular shaped composites has been very limited. The mechanical properties of one filament wound 3.8 cm diameter (6 mm wall thickness) tubular composite have been measured. The 16 cm long tubular composite was cut into 6 mm thick C-ring specimens. Room temperature compression testing of three of these rings ranged from 777 MPa to 842 MPa. Testing at 1000°C resulted in slightly lower strengths that ranged from 574 to 603 MPa. Composites reinforced with braided or filament wound preforms are currently being fabricated for tension/torsion testing at room and elevated temperature.

CONCLUSIONS

Fiber-reinforced SiC matrix composites of tubular geometry are desired for application in advanced gas turbines because of their oxidation resistance, damage tolerance, and thermal shock resistance. A process has been developed that can efficiently fabricate thick-walled tubes in short times without damaging the reinforcing fibers. Tubular preforms were obtained with different fiber architectures to satisfy different strength requirements. Densification of filament wound tubes was accomplished without difficulty because the tubular preforms were sufficiently permeable to disperse the reactants along the length of the preform. Infiltration then proceeded as desired from the hot face to the cool face of the preform. Densification of braided preforms was considerably more difficult. Braided preforms were less dense and had porosity that extended through the walls. Therefore, the preforms were so permeable that reactants failed to disperse properly along the length of the

preform. After denser, much less permeable braided preforms were obtained, densification of tubular preforms was achieved. C-ring strengths of filament wound composites were found to be quite high (~800 MPa) at room temperature but decreased to ~600 MPa at 1000°C.

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2.2 ALTERNATE INTERFACE COATINGS FOR NICALON®/SiC COMPOSITES

R. A. Lowden and O. J. Schwarz

INTRODUCTION

Boron doping of the carbon interface coating was examined to improve the elevated-temperature stability of Nicalon®/SiC composites. Boron trichloride (BCl_3) was added to the hydrocarbon gas mixtures during the deposition of the fiber coatings. Two carbon precursor gases, propylene and methane, were explored. The coated preforms were densified with a silicon carbide matrix using the forced-flow, thermal-gradient chemical vapor infiltration process. Room temperature flexure strengths of as-fabricated composites, and specimens exposed to 1273 K in air for 24 h, were measured to assess the oxidation behavior of the interlayers. Small additions of boron to the carbon interface coating improved the oxidation resistance of the composites without affecting mechanical properties. Higher boron concentrations, however, degraded the strength and toughness of the materials.

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. Nicalon®/SiC composites with a graphitic carbon interface layer exhibit properties favorable for use in fossil energy applications, and thus have 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 a variety of combustion environments at elevated temperatures. The mechanical properties of unprotected Nicalon®/SiC specimens were degraded after short periods of exposure, due to the oxidation 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. Combustion environments hastened the embrittlement of the composites.

Nicalon®, Nippon Carbon Company, Tokyo, Japan.

The specimens protected by a SiC surface coating exhibited no decrease in strength after exposure to oxidative or combustion environments. The SiC layer sealed off the surface of the composites, protecting the exposed fibers' ends, and thus prohibiting oxidation at the fiber-matrix interface. The surface coating was essential to protect the 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. It is generally accepted that these surface protection measures are only one component of a more complex protection system. A complete system may require combinations of surface layers, oxidation inhibitors, and fiber coatings.

These issues must be addressed in the development of environmentally-stable ceramic composites. If volatile interlayers are to be used, there exists a need to develop more oxidation resistant fiber coatings for use in ceramic matrix composites. 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 stability of carbonaceous materials, such as structural graphite and carbon-carbon composites. These efforts have focused on the development of glass forming materials, specifically glasses with melting temperatures and viscosities lower than that of pure silica. Silica functions well as a surface coating at higher temperatures (>1500 K) but SiO_2 glass does not flow at lower temperatures limiting its effectiveness. Boron is the most frequently studied addition for temperatures around 1273 K.⁹⁻¹¹ Boron forms a lower melting point glass ($T_m \sim 725$ K) that flows more readily to seal the surface of the material and slow further attack of the substrate.

This paper describes efforts to apply oxidation inhibitor concepts to interface coatings for Nicalon®/SiC composites. Boron-doping of the carbon interface layer was examined to improve the oxidation resistance of the composites. The short-term oxidation resistance of the composites was used to determine minimum dopant levels and assess the effectiveness of boron-doped carbon as an improved interface coating for Nicalon®/SiC composites.

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 nominal size of the fibrous preforms was 45 mm in diameter and 12.5 mm thick.

Preforms were then coated with boron-doped carbon interface layers. The coatings were deposited isothermally at 1375 K and 3.3 kPa from gas mixtures containing a hydrocarbon gas, argon, and boron trichloride (BCl_3). Two carbon precursor gases were examined, propylene and methane. Control samples with no boron were first prepared and then BCl_3 was introduced to the gas mixture to produce boron-containing dispersions in the carbon layer. Reactant flows and concentrations were adjusted to produce deposition rates comparable to those of the standard graphitic carbon layer, and to produce a uniform layer throughout the preform. The amount of boron in the layer was varied by altering the composition of the coating gas mixtures (Table 1). Layer deposition times were 2 h which produced coatings thicknesses of $\sim 0.3 \mu\text{m}$. The thicknesses of the interface layers were calculated from weight gains.

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.^{1,12-14} 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.

Characterization and Testing

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 $2.5 \times 3 \times 40$ mm and all specimens were measured and weighed to determine densities.

Table 1. Interface coating deposition parameters.

CVI Number	Hydrocarbon Flow (sccm)	BCl ₃ Flow (sccm)	Argon Diluent (sccm)	Weight Gain (g)	C:B Ratio in Gas Mixture
<i>Propylene</i>					
584	25	0	500	1.5	---
585	25	2	500	1.2	37.5
586	25	5	500	1.4	15.0
587	25	10	500	1.5	7.5
588	25	20	500	1.8	3.8
589	20	25	500	1.5	2.4
599	10	25	500	2.3	1.2
591	5	25	500	1.7	0.6
<i>Methane</i>					
604	720	0	0	1.5	---
607	720	5	0	2.3	144
610	360	5	140	2.3	72
611	180	5	320	1.8	36
612	90	5	410	1.5	18

Half of the specimens were oxidized in static air at 1273 K for 24 hours. 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. A support span of 25 mm and a loading span of 6 mm were used with a crosshead speed of 0.50 mm/min. 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.

RESULTS

Mechanical Properties

Typical load-displacement curves for the Nicalon®/SiC composites with propylene-derived interface coatings are shown in Figure 1. The composites with no or small boron additions exhibited good strength and composite behavior, ie. failed gradually with extensive fiber pull-out. The strength and toughness of the composites was diminished at the higher boron concentrations. Failure became more brittle and catastrophic at the highest boron additions as noted by the load-displacement curve also shown in Figure 1.

Fig. 1. Representative load-deflection curves for composites with propylene-derived interface coatings. [Curves are offset horizontally for clarity.]

The composites fabricated with interface layers deposited from methane gas mixtures also exhibited high strength and gradual failure. The deleterious effects of higher boron

concentrations on mechanical properties were noted in the experiments with propylene, and thus only small boron additions were examined. Representative flexure curves for this series of composites are given in Figure 2.

Fig. 2. Representative load-deflection curves for composites with methane-derived interface coatings. [Curves are offset horizontally for clarity.]

Oxidation

Exposure to 1273 K in air for 24 h produced a slight discoloration of all specimens suggesting some degree of surface oxidation. The specimens fabricated with carbon interface coatings that did not contain boron exhibited significant losses in flexure strength after the short-term exposure (Figures 3 and 4). Beyond a minimum concentration, the addition of boron resulted in an improvement in strength retention for composites with propylene- and methane-derived interface coatings. This minimum boron addition corresponded to a carbon to boron ratio between 15 and 37.5 for the propylene coatings, and 18 and 36 for the methane deposits. At these boron concentrations, the composites exhibited no change in mechanical properties after oxidation. Although higher concentrations of boron produced decreases in strength and toughness for the composites with interlayers deposited from propylene mixtures, the mechanical properties of the composites were also unaffected by oxidation.

Fig. 3. Flexure strength comparison of as-fabricated and oxidized composites with propylene-derived interface coatings.

Fig. 4. Flexure strength comparison of as-fabricated and oxidized composites with propylene-derived interface coatings.

DISCUSSION

Carbon is currently used as an interface coating in a number of ceramic composite systems.^{1,2,15} The carbon fiber coatings are employed to protect the reinforcements during processing, and to control bonding and friction at the fiber-matrix interface. Exceptional room- and elevated-temperature mechanical properties have been measured, and these composites are prime candidates for use in many advanced elevated-temperature applications. Nevertheless, the poor oxidation resistance of carbon is well known, as is the fact that any disturbance of the fiber-matrix interface can have profound effects on the properties of a composite.³⁻⁵

It has been shown that the oxidation of Nicalon®/SiC composites with a graphitic carbon interlayer begins by attack of the interface coating at exposed fiber ends.^{6,7} With the fibers lying in one plane, oxidation at lower temperatures proceeds along the fiber lengths. As the carbon interlayer oxidizes, carbon is in equilibrium with carbon monoxide, and thus a high carbon potential is maintained along the fiber-matrix interface. Oxidation of the fibers and matrix is therefore hindered. Once the carbon is removed along the entire fiber length, the matrix and fiber oxidize to form a silica layer that eventually bonds the components together. The strong bond at the fiber-matrix interface does not permit debonding and sliding, resulting in brittle behavior. Also, oxidation degrades the properties of the fiber, enhancing the embrittlement of the composite.

In contrast, the carbon interlayer was not attacked in specimens with a SiC surface coating even after 1000 hours. The ends of the fibers and the fiber-matrix interface layer were not exposed, thus hindering oxidation of the carbon interlayer and composite constituents. Although the SiC surface coating provided protection for the carbon interface layer, the effectiveness of surface layers can be limited. As discussed earlier, processing flaws, or cracks in the coating caused by thermal expansion mismatch stresses or applied loads can expose the underlying fiber coatings, leaving said susceptible to oxidation. A solution to such problems is to improve the oxidation resistance of the fiber coating and/or utilize a fiber coating with "self-healing" capabilities.

Glasses are the primary materials employed as surface coatings and crack sealants for carbonaceous materials.⁸ Glasses have low oxygen permeability, and can melt and flow to completely cover and seal surfaces and cracks. The glass former that has been most effectively utilized is boron. Boron has long been a key ingredient in oxidation resistant

graphite and carbon-carbon composites. Boron oxidizes to form boria (B_2O_3) which melts at 725 K, allowing the glass to flow at temperatures relevant to many applications of interest for Nicalon®/SiC composites.

The mechanisms by which boria protects carbon from oxidation have been the subject of many studies.⁹⁻¹¹ Two protection mechanisms have been suggested; each of which is dependent upon the concentration of boron in the carbonaceous substrate. It has been shown that the minimum boron concentration for improvement in oxidation resistance is $\sim 2\%$.^{9,10} For low boron concentrations, the B_2O_3 segregates to active oxidation sites, where the glass shields these sites from exposure, and retards further oxidation.⁹ At higher boron levels, a thin continuous glass film is formed, hindering diffusion of oxygen and deterring further oxidation of the carbon substrate.^{10,11}

Using post-exposure flexure strength as a measure of effectiveness, the oxidation of the carbon interlayer was inhibited when the concentration of boron in the reactant gas mixture was between 2.5 and 7 vol %, in excellent agreement with the aforementioned efforts. Investigation of the deposition of boron carbide has shown that, using gas mixtures similar to those in this study, the deposition of boron was hindered without the addition of hydrogen to assist in the decomposition of BCl_3 .¹⁶⁻¹⁹ Coatings produced from BCl_3 and hydrocarbon gas mixtures generally have boron concentrations less than predicted from the initial reactant gas composition. Therefore, the concentration of boron in the interface coatings was most likely less than what would be expected from perfect deposition efficiency, explaining the negligible difference between the results of this study and earlier work.

The compositions and microstructures of the coatings have not been characterized, however, it is speculated that the boron should be present in the form of B_4C . The deposition of boron carbides from BCl_3 and hydrocarbon gases has shown for boron concentrations of $< 0.4\%$, boron is in solid solution with carbon.^{18,19} At higher concentrations, boron was found as B_4C dispersed uniformly throughout the deposit. Pure B_4C was deposited as the carbon to boron ratio in the reactant gas mixture approaches unity.

Higher levels of boron in the coatings produced brittle composites with low strength. The addition of boron to CVD carbon increases the strength, modulus, and hardness of the material.¹⁹ The strength and toughness of the Nicalon®/SiC composites decreased with increased boron concentration. These reductions in mechanical properties have been attributed to changes at the fiber-matrix interface. The thicknesses of the coatings were

nearly constant, thus it is hypothesized that as more boron was added to the interlayer, its properties were altered. The interface layer became harder and stiffer. The soft, low modulus layer that was able to accommodate a portion of the residual clamping stresses at the interface was replaced with a hard, stiff boron carbide coating. Interfacial shear and frictional stresses were thus altered²⁰, explaining the reductions in strength and toughness of the composites.

CONCLUSIONS

Boron doping of the carbon interlayer proved to be an effective method for improving the short-term oxidation resistance of the Nicalon®/SiC composites. Boron concentrations as low as 1 % in the gas mixture produced notable improvements in post-exposure strength retention. The boron was added to inhibit oxidation of the interface coating through the formation of a glass layer that could seal the exposed surfaces of the fiber coating and prevent further attack. Small concentrations of boron had little effect on the mechanical behavior of the composites, however, properties were diminished at higher dopant levels. The interface coating becomes stiffer and hard with increasing boron content, therefore interfacial forces are altered, resulting in a loss of strength and embrittlement of the material.

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2.3 MICROWAVE SINTERING OF ZIRCONIA

M. A. Janney, M. L. Jackson and H. D. Kimrey

INTRODUCTION

The study of microwave processing of ceramic materials at ORNL has shown that some materials exhibit a significant "microwave effect" but that others exhibit little or no "microwave effect." (The "microwave effect" is manifested as lower temperature sintering or faster kinetics at a given temperature.) Alumina, zirconia, alumina-zirconia composites, lithium hydride, and silicon nitride have been demonstrated to exhibit significant microwave effects in sintering, grain growth, and diffusion. Lanthanum chromite, 123 superconductor, boron carbide, and titanium diboride exhibit little if any microwave effect. The most significant difference between these two groups of materials is their electrical conductivity. The first group consists of ionic conductors and insulators; the second group consists of electronic conductors. It is proposed that the ratio of ionic conductivity to electronic conductivity, (s_i/s_e) is a controlling factor in determining whether or not a system exhibits a microwave effect. Furthermore, it has been observed that in systems having low electronic conductivity, the magnitude of the microwave effect appears to be greater as the ionic conductivity increases. The purpose of the current investigation is to investigate both of these hypotheses in a single materials system. The system chosen for study is the $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$ system.

The $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$ system is attractive for study for a number of reasons. Its total electrical conductivity can be varied over several orders of magnitude. Its conductivity can be altered from being predominantly ionic to predominantly electronic in nature. The addition of Y_2O_3 to the system provides a means to fix the level of ionic conductivity in the system by the creation of oxygen vacancies. Electronic conductivity can be adjusted by varying the partial pressure of oxygen in the processing furnace, which reduces Ce^{+4} to Ce^{+3} and establishes electron charge carriers in the material.

An investigation of the role that ionic and electronic conductivity play in determining the "microwave effect" has been initiated. Initial tests have been made with $\text{ZrO}_2\text{-12 mol\%}$

CeO₂. Subsequent studies will be conducted using yttria levels between 0.1 and 3 mol% and a ceria level of ~18 mol%.

Experimental Procedure

The insulation system used for the microwave firing of ZrO₂-12 mol% CeO₂ is shown in Fig. 1. The system uses the "picket fence" approach originally developed for the firing of ZrO₂-8 mol% Y₂O₃. The sample is separated from the zirconia bulk fiber insulation by a porous alumina crucible, which acts as a physical barrier to prevent contact between the ZrO₂-12 mol% CeO₂ sample and the zirconia fiber. The zirconia bulk fiber insulation has a composition of ZrO₂ - 8 mol% Y₂O₃ and contamination of the ZrO₂-12 mol% CeO₂ with yttria from the insulation is not desired. The combination of the SiC pickets and the zirconia bulk fiber insulation provides a means to heat the ZrO₂-12 mol% CeO₂ samples in a uniform and repeatable manner.

Figure 1. Schematic of "picket fence" insulation system for ZrO₂ microwave sintering.

RESULTS AND DISCUSSION

Sintering results for ZrO₂-12 mol% CeO₂ in air in the microwave and conventional furnaces is shown in Fig. 2. There is a shift in the sintering curve of about 60°C between the microwave and the conventional sintering results. This shift is smaller than that observed previously in the sintering of ZrO₂-8 mol% Y₂O₃. The reason for the smaller microwave effect is thought to be the lower ionic conductivity of the ZrO₂-12 mol% CeO₂ compared

with that of the ZrO_2 -8 mol% Y_2O_3 . Additional experiments in the ZrO_2 - CeO_2 - Y_2O_3 system will confirm or deny this hypothesis in the future.

Fig. 2. Sintering of ZrO_2 -12 mol% CeO_2 in air in microwave and conventional furnaces.

Initial results from the sintering of ZrO_2 -12 mol% CeO_2 in both air and reducing atmosphere (N_2 -4% H_2) are shown in Fig. 3. The ZrO_2 -12 mol% CeO_2 samples sintered better in air than in reducing atmosphere. These initial results tend to confirm our hypothesis regarding the role of electronic conductivity in microwave sintering. The samples fired in reducing atmosphere did not sinter as well as those fired in air. However, conventional sintering experiments in reducing atmosphere have not as yet been completed, so no true side-by-side comparison can be made at this time.

Fig. 3. Microwave sintering of ZrO_2 -12 mol% CeO_2 in air and N_2 -4 H_2 .

SUMMARY AND CONCLUSIONS

Initial sintering results on the system ZrO_2 -12 mol% CeO_2 indicate that both the total ionic conductivity in a material and the ratio of ionic to electronic conductivity are important in determining the magnitude of the microwave effect in that material. For sintering in air, ZrO_2 -12 mol% CeO_2 exhibited a smaller microwave effect than did ZrO_2 -8 mol% Y_2O_3 which was investigated earlier. The ceria-doped zirconia has a lower conductivity than the yttria-doped material; these results lend support to the importance of the total ionic conductivity in microwave processing. For microwave sintering in air and N_2 -4% H_2 , the material fired in air sintered better than that fired in N_2 -4% H_2 . These results support the hypothesis that high electronic conductivity impedes the microwave effect.

2.4 FABRICATION AND PROCESSING OF IRON ALUMINIDES

V. K. Sikka and S. Viswanathan

INTRODUCTION

The Fe_3Al -based alloys have been shown to exhibit room-temperature ductility values of 15 to 19% by the control of composition and thermomechanical processing steps. The scale-up of one of the compositions to 2270-kg (5000-lb) electroslag-remelted (ESR) round ingot and 3272-kg (7200-lb) vacuum-induction-melted (VIM) slab ingot is described. Microstructural and mechanical property data are presented on small pieces sectioned from these ingots. The effects of final rolling temperature and the final annealing treatment on room-temperature ductility were investigated for the ESR ingot. A study of iron-aluminide binary alloys revealed that the environmental effects on room-temperature ductility values were absent for ≤ 8.5 wt % Al. The increasing aluminum content and the development of ordered structure resulted in increased environmental effects. Applications and a brief description of their status are described. Based on the combined property and cost advantage, continued development of iron aluminide is recommended.

The Fe_3Al -based iron-aluminide alloys offer excellent resistance in carburizing, sulfidizing, and oxidizing environments. The resistance to these environments is superior to many commercially used iron- and nickel-based alloys at temperatures in the range of 600 to 1200°C. The poor room-temperature ductility of Fe_3Al -based alloys has been the major limitation in the use of these materials for almost 100 years. The recent advances in understanding the causes of poor room-temperature ductility of these alloys have triggered a strong interest in their applications. The ductility of Fe_3Al -based iron-aluminides has been significantly improved through composition modification and controlled thermo-mechanical processing. Several publications¹⁻⁸ have dealt with the development of ductile compositions, thermomechanical processing requirements, melting procedures, environmental effects on ductility, mechanical properties, oxidation and sulfidation resistance, and corrosion resistance. The purpose of this paper is to: (1) provide an update on progress made towards commercial melting, processing, and mechanical properties of select compositions, (2) report

recent developments toward reducing the environmental effects on room-temperature ductility, and (3) report the status of iron-aluminide applications.

Commercial Melting, Processing, and Mechanical Properties of Select Compositions

Three compositions (Table 1) of Fe₃Al-based alloys have been chosen for commercial applications. The key reason for choosing each composition is also indicated in Table 1. The FAS composition is being considered for its excellent sulfidation and oxidation resistance. Powder of the FAS composition is being commercially produced and sold by Ametek Specialty Metal Products Division (Eighty Four, Pennsylvania). The alloy composition is melted in air and atomized into powder by nitrogen gas. Consolidation has been carried out by hot-isostatic pressing or hot extrusion. The properties of powder consolidates are available in previous publications.^{9,10} Testing of FAS powder for oxidation- and sulfidation-resistant coatings on various substrates is currently in progress.

Table 1. Compositions of ductile, Fe₃Al-based alloy

Element	Alloy (wt %)		
	FAS ^a	FAL ^b	FA-129 ^c
Al	15.9	15.9	15.9
Cr	2.20	5.5	5.5
B	0.01	0.01	--
Zr	--	0.15	--
Nb	--	--	1.0
C	--	--	0.05
Fe	Balance	Balance	Balance

^aMaximum sulfidation resistance.

^bMaximum room-temperature tensile ductility.

^cHigh-temperature tensile strength with good room-temperature ductility.

The FAL composition, developed for maximum room-temperature ductility, has been scaled up² into a 203-mm-diam ingot at Carpenter Technology Corporation (Reading, Pennsylvania). Because of its poor weldability, further work on the FAL alloy has been on hold. The main effort on commercial scale-up has been focused on alloy FA-129. Ingots of

152-mm-diam were processed by VIM, followed by either the vacuum-arc remelting (VAR) or the ESR process, at Special Metals Corporation (New Hartford, New York). Precision Rolled Products (PRP) (Reno, Nevada) prepared approximately 2270 kg (5000 lb) of the alloy by the VIM process. A 330-mm-diam ingot was cast and used as an electrode for ESR melting into a 406-mm-diam by 2.77-m-long ingot (Fig. 1). The surface quality of the ingot was excellent.

ORNL PHOTO 3603-92

Fig. 1. Photograph of a 406-mm-diam by 2.77-m-long ingot of alloy FA-129 vacuum-induction melted and electroslag remelted by Precision Rolled Products.

Precision Rolled Products VIM processed an additional 3272-kg (7200-lb) heat of FA-129 and cast a slab (Fig. 2), 203 mm $\times$ 965 mm $\times$ 2.54 m, of good surface quality. The check chemical analysis of the ESR ingot and the VIM slab are compared with the target chemistry in Table 2. All of the elements in the commercial-size ESR ingot and VIM slab met the specified range for alloy FA-129. Also, the ESR process reduced the sulfur content of the VIM ingot from 0.008 to 0.001 wt %. The nitrogen content of both ingots was extremely low, 0.0001 wt %. The oxygen content of the ESR and VIM ingots were 0.0015 and 0.0010 wt %, respectively. Based on these data, the chemical specification for alloy FA-129 should be achievable during commercial scale-up.

Commercial vendors cut a 28-mm-thick slice from the top of the 406-mm-diam ESR ingot using a band saw and a second slice of 127-mm thickness using an abrasive cutoff wheel. Subsequent pieces were cut with a band saw at the Oak Ridge National Laboratory.

Small sections from the ESR- and VIM-processed FA-129 ingots were examined metal-lographically. The photomicrographs of the unetched surfaces (Fig. 3) show that the ESR ingot possessed very limited porosity of a very small size. The VIM ingot contained more porosity and of a larger size than the ESR ingot. Furthermore, the last eutectic to

freeze in the ESR ingot had a much finer distribution than that of the VIM ingot. The observed microstructural features of the ESR ingot are consistent with its smaller melt pool and higher cooling rates. The VIM slab ingot cooled at a much slower cooling rate because its entire volume was molten at one time.

ORNL PHOTO 3604-92

Fig. 2. Photograph of a 203-mm $\times$ 965-mm $\times$ 2.54-m slab ingot of alloy FA-129 vacuum-induction melted at Precision Rolled Products.

ORNL Photo 3605-92

(a)

(b)

Fig. 3. Optical microstructure in unetched condition of sections cut from the 2270-kg electroslog-remelting round ingot: (a) 3272-kg vacuum-induction-melted slab ingot and (b) of alloy A-129. Both ingots were prepared at Precision Rolled Products.

Table 2. Comparison of chemical analysis of a 406-mm-diam electroslag-remelting ingot and a 203-mm-thick vacuum-induction-melted slab of iron-aluminide alloy FA-129

Element	Target	Weight percent		
		Range	Check analysis ^a	
			406-mm-diam ESR ingot	203-mm-thick VIM slab
C	0.05	0.04-0.06	0.050	0.047
Mn	--	0.20 Max.	0.25	0.17
P	--	0.005 Max.	0.011	0.009
S	--	0.005 Max.	0.001	0.008
Si	--	0.20 Max.	0.09	0.06
Ni	--	0.20 Max.	0.07	0.07
B	--	0.005 Max	--	--
Mg	--	0.0010 Max	--	--
N	--	0.0050 Max.	0.0001	0.0001
O	--	0.0050 Max.	0.0015	0.0010
Al	15.9	15.5-16.5	16.45	15.93
Cr	5.5	5-6	5.76	5.62
Nb	1.0	0.9-1.1	1.06	1.18
Fe	77.55	Balance	76.7	77.1
Zr	--	--	<0.01	0.01
Mo	--	--	<0.01	0.01

^aConducted at ABB Combustion Engineering Systems, Chattanooga, TN.

Two 28- ¥ 76- ¥ 102-mm sections from the 28-mm-thick slice were processed into a 0.76-mm-thick sheet. The processing steps used for the two pieces are shown systematically in Fig. 4. The six temperatures used for the last 70% reduction were 450, 500, 650, 700, 800, and 900°C. All of the sheets were stress relieved at 700°C for 1 h and quenched in mineral oil. All of the specimens were annealed at 700°C for 1 h and either air cooled or quenched in mineral oil, except that one set of specimens was given a final anneal at 900°C for 1 h, followed by quenching in mineral oil. Specimens from sheets final rolled at various temperatures were tested at room temperature and at a strain rate of $3.3 \times 10^{-3} \text{ s}^{-1}$ (0.2/min). Specimens from sheets final rolled at 700°C with a final heat treatment at 700°C for 1 h and quenched in mineral oil to room temperature were tensile tested at 100, 200, 400, 600, and 800°C.

Fig. 4. Schematic showing steps in the processing of sections from the 406-mm-diam electroslag-remelted ingot of FA-129.

Room-temperature tensile properties of the ESR ingot of alloy FA-129 are plotted as a function of final rolling temperature in Fig. 5. The plots show that the final annealing temperature and cooling medium affect the room-temperature tensile properties more than the final rolling temperature. For a final annealing temperature of 700°C, the oil quenching produced higher values of ultimate tensile strength, total elongation, and reduction of area values than air cooling. The 0.2% yield strength was not affected by the final cooling media. For cooling from the annealing temperature by quenching in mineral oil, the annealing temperature of 900°C produced lower values of both strength and ductility than the annealing temperature of 700°C. The higher annealing temperature of 900°C had a much less effect than the final rolling temperature. The detailed metallography of the specimens with final rolling at various temperatures are available elsewhere.¹¹

The higher ultimate tensile strength and ductility values for samples that are oil quenched are associated with an environmental effect.^{4,5} The oil quenching prevents hydrogen generation from the reaction of aluminum in the alloy with moisture in air by acting as a barrier between the specimen surface and the environment. The coarser grain structure in specimens annealed at 900°C produces further reduction in ductility, a consequence of the Hall-Petch effect. The study in Fig. 5 showed that high, room-temperature ductility values in alloy FA-129 can be obtained by final rolling in the temperature range of 500 to 700°C.

Fig. 5. Tensile properties at room temperature as a function of final rolling temperature for alloy FA-129: (a) yield strength, (b) ultimate tensile strength, (c) total elongation, and (d) reduction in area.

Tensile properties of the sheet prepared from the 406-mm-diam ESR ingot are compared with that of the sheet prepared from the 101-mm-diam VIM ingot in Fig. 6. The 101-mm-diam VIM ingot was tested in air after cooling from the annealing temperature by quenching in mineral oil or in air. The air-cooled specimens were also tested in vacuum. The specimens from the 406-mm-diam ingot were tested only after quenching in mineral oil from the annealing temperature. The annealing temperature of 700°C and time of 1 h were

the same for all of the specimens. The ultimate tensile strength and the ductility values were lower for the 406-mm-diam ingot than those for the 101-mm-diam ingot for test temperatures of $\leq 400^{\circ}\text{C}$. These values were especially lower for the test temperature of 100°C . The exact reasons for this behavior are not clear at present.

ORNL DWG 92-9015

Fig. 6. Comparison of tensile properties of sheet processed from a 406-mm-diam electroslag-remelted ingot from Precision Rolled Products with sheet processed from a 101-mm-diam vacuum-induction-melted ingot from Special Metals Corporation. All of the sheets were processed identically and given a final anneal at 700°C for 1 h.

Room-temperature tensile properties of the VIM slab are compared with the ESR ingot of alloy FA-129 in Fig. 7. The room-temperature properties of the VIM and ESR ingots are nearly the same. Slightly more scatter in the data for the VIM ingot is considered to result from its somewhat larger size porosity, which might not have completely closed during processing.

ORNL DWG 92-9016

Fig. 7. Comparison of room-temperature tensile properties of sheets processed from a 2270-kg (5000-lb) electroslog-remelted round ingot and a 3272-kg (2700-lb) vacuum-induction-melted slab ingot. Sections from both ingots were processed and heat treated identically.

The results of Figs. 6 and 7 show that the commercial scale-up of alloy FA-129 to ingot sizes of 3272 kg lowers the ultimate tensile strength and ductility values for test temperatures of $<400^{\circ}\text{C}$, as compared to the experimental size heats.

Environmental Effects

The environmental effects are considered as the main cause for poor room-temperature ductility of iron aluminides. A systematic investigation of aluminum addition on room-temperature ductility in binary FeAl alloys was conducted.¹² The binary alloys were prepared in disordered, fully ordered, and in the ordered/disordered ranges of the phase diagram. All of the alloy heats were of the same size, prepared by nonconsumable

melting, and processed identically to 0.76-mm-thick sheet. The sheets were given a stress relief of 700°C for 1 h followed by quenching in oil. The punched specimens were given a final anneal of 700°C for 1 h followed by air cooling. The oil-quenched samples were tested in air and in vacuum. Two of the five alloys were not tested in vacuum.

The effect of test temperature on room-temperature total elongation for various aluminum-containing binary alloys is compared in Fig. 8(a and b). The bar charts in Fig. 8(a) shows that the total elongation values in vacuum for air-cooled samples are the same as those observed for oil-quenched samples tested in air for aluminum contents of 12 and 15.9 wt %. This implies that the oil film on the oil-quenched samples provides the same protection from the environmental effect (hydrogen generation) as vacuum. However, for the disordered composition of 8.5 wt % Al, ductility values of air-cooled samples tested in air and vacuum are the same and the oil-quenched samples are somewhat lower. These results imply that the 8.5 wt % Al binary is not sensitive to environmental effects. The room-temperature ductility results for five different aluminum levels are compared for oil-quenched and air-cooled samples in Fig. 8(b). The boundaries for the disordered α phase, the two-phase disordered α and ordered $D0_3$, and the single-phase ordered $D0_3$ are also shown in Fig. 8(b). Note that tensile ductility values for the ordered alloy are higher for the oil-quenched samples than the air-cooled samples. For the disordered region, the air-cooled

Fig. 8. Effect of aluminum on room-temperature ductility of binary iron-aluminide alloys: (a) bar charts comparing effect of testing in air and vacuum, and (b) plot showing the effect of cooling media.

samples have higher values than the oil-quenched samples. In the two-phase material, the oil-quenched and air-cooled samples have similar values.

The results of Fig. 8(a and b) show that environmental effects for iron-aluminide alloys are magnified by increasing the aluminum content and by producing ordered structure. A new alloy composition based on 8.5 wt % Al content is being developed with For the disordered region, the air-cooled samples have higher values than the oil-quenched samples. In the two-phase material, the oil-quenched and air-cooled samples have similar values. room-temperature total elongation values of 25 to 28%. The environmental effect is greatly reduced, and these compositions still possess better oxidation and sulfidation resistance than many commercial alloys.¹³

Status of Applications

Iron aluminides are being pursued for applications where high-temperature oxidation, sulfidation, and carburization resistance are required. These include porous gas-metal filters for hot-gas cleanup in coal gasification systems, furnace furniture, heating elements, coatings for oxidation and sulfidation, automotive exhaust parts, and potentially molten aluminum resistance. The fabrication procedures, properties data, and prototype testing are under way for several of the applications mentioned above. The low ductility in the cast condition, additional information on cutting and machining, welding procedure and electrode development, fabrication process development, property data of fabricated prototypes, and the cost data are still considered deterrents to near-term commercialization of Fe₃Al-based alloys. With the new knowledge on aluminum levels for absence of environmental effects and higher room-temperature ductility, the lower aluminum-based iron-aluminide alloys may help reduce the commercialization time for some applications. The iron-aluminide alloys show combined benefits of property and cost advantages and, thus, their further development needs continued.

Summary and Conclusions

The Fe₃Al-based FA-129 alloy was commercially melted into a 406-mm-diam and 2270-kg (5000-lb) ingot by the ESR process at PRP. A 203-mm × 965-mm × 2.54-m slab ingot weighing 3272-kg (7200 lb) was also prepared by the VIM process at PRP. Sections from these ingots were subjected to metallography and thermomechanical processing to produce 0.76-mm-thick sheets for mechanical properties evaluation. A study was carried out

to determine the effect of final rolling temperature and heat-treatment conditions on room-temperature tensile properties. The tensile properties were generated as a function of temperature for the 406-mm-diam ingot and compared with the previously tested 101-mm-diam ingots. Room-temperature tensile properties were compared for the ESR ingot and the VIM slab.

A study was conducted on the binary iron-aluminide alloys to determine the aluminum levels for minimizing the environmental effect on room-temperature ductility. The following conclusions are possible from this work:

1. The ESR ingot showed much less porosity than the VIM ingot. The ESR ingot also showed much finer distribution of the last liquid to freeze than the VIM ingot.
2. A final rolling temperature in the range of 500 to 700°C followed by annealing at 700°C and quenching in mineral oil can be used to produce high, room-temperature ductility values for alloy FA-129. Oil provides a barrier to the generation of hydrogen on the surface from the reaction of aluminum in the alloy and moisture in the air.
3. The ultimate tensile strength and ductility values of commercial-size ingots were lower than those of the 101-mm-diam ingot for test temperatures of <400°C. The exact reasons for this behavior are not clear at present.
4. The environmental effects for the iron-aluminide alloys are enhanced by increasing the aluminum content and by producing ordered structure. A binary alloy containing 8.5-wt-% Al and a disordered structure resulted in total elongation values of 25 to 28% and the absence of effects from testing in air or vacuum.

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2.5 SOLIDIFICATION BEHAVIOR OF FA-129 IRON-ALUMINIDE ALLOY

S. Viswanathan, P. J. Maziasz and V. K. Sikka

INTRODUCTION

Samples of FA-129 iron-aluminide alloy have been processed by various casting processes, including vacuum arc-melting followed by chill casting into water-cooled copper molds, air melting followed by casting into graphite molds, and electroslog melting and casting into large ingots. The resulting microstructures obtained in these processes are examined and compared. Selected samples are homogenized at various temperatures and times. Optical and transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) are used to identify the morphology, constituents, and compositions of various phases. Interrupted solidification experiments are used to study the evolution of cast structure. Some observations are made on the effect of dissolved hydrogen in the melt on as-cast soundness.

Applications for Fe₃Al-based iron-aluminide alloys include steam turbine parts, heating elements, automotive exhaust systems, components in sulfidizing environments, and components in highly oxidizing environments such as containment for molten salts, furnace furniture, and gas filters.¹ The initial development effort¹ at the Oak Ridge National Laboratory was conducted on material processed from 350-g ingots arc melted and drop cast into water-cooled copper molds. Further development was conducted on 7-kg air- and vacuum-induction melts (AIM and VIM). Larger heats of 50 to 2700-kg have also been produced through commercial vendors.² However, processing of the 2700-kg ingot, in particular, has been difficult due to the presence of hot-tears formed during solidification. Also, notched-impact properties of specimens obtained from 13-mm plates produced from the larger heats have been poor due to fracture initiation at second-phase particles.³ Consequently, a detailed study has been undertaken to characterize the cast microstructure, phase constituents, casting and processing variables, hot-tearing tendency, and material properties of FA-129 alloy. The results of the study will be applicable to other iron-aluminide alloys and should facilitate development of better properties in iron-aluminide alloy components.

DISCUSSION OF CURRENT ACTIVITIES

Characterization of As-Cast Structure

Samples of FA-129 alloy cast by three different processes were examined metallographically. The alloy to be drop cast was initially arc melted under an argon pressure of 0.07 MPa (580-mm Hg) in a water-cooled copper crucible. The buttons were remelted six times to ensure homogeneity, and drop cast into a water-cooled copper mold to form 25- $\times$ 12- $\times$ 125-mm ingots. Figure 1(a) shows the microstructure obtained in a sample taken from the top of the ingot. Examination of the cast structure reveals the presence of two types of second-phase particles, the first distributed within the grain and consisting of a "rod" morphology, and the second present at the as-cast grain boundaries in a "globular" interdendritic morphology. The globular particles, based on their location of occurrence, would be expected to have been precipitated from the "last liquid to freeze."

Figure 1(b) shows the microstructure obtained in FA-129 alloy cast in a graphite slab mold. The alloy was melted in an AIM furnace and poured into a 2.5- $\times$ 10- $\times$ 15-cm graphite slab mold preheated to 300°C. The microstructure obtained in the slab ingot is very similar to that obtained in the chill-cast ingot. Table 1 shows the chemical analysis obtained for the slab ingot. Figure 1(c) shows the microstructure obtained in a 2700-kg, electroslag-remelted ingot. Again, two types of second-phase particles are observed, although both the particle size and the spacing between particles increases as the solidification time of the ingot increases. It should be noted that the morphology of the particles, which seemed to initiate cleavage fracture in another study,³ is very similar to the "rods" observed in the as-cast structure. Therefore, the origin and nature of the second-phase particles observed in the as-cast alloy were investigated in more detail.

Table 1. Chemical composition of slab ingot (wt %)

Fe	Al	Cr	Nb	C	Mo	Zr	S
78.0	15.75	5.38	0.78	0.038	<0.01	<0.001	0.002

Fig. 1. Optical micrographs of FA-129 alloy: (a) 350-g ingot "chill-cast" in a water-cooled copper mold, (b) 7-kg ingot cast in a graphite mold, and (c) 2700-kg electroslag-remelted ingot. Note the change in magnification in (c).

TEM micrographs were obtained for as-cast specimens. Figure 2(a) shows a TEM micrograph of a rod shaped precipitate. The TEM analysis indicates that the large rods viewed by SEM or optical metallography appear to be clusters of smaller rods or laths, rather than a single precipitate. Figure 2(b) shows a bright field image of antiphase boundaries (APBs) separating the small D0_3 domains in the as-cast alloy. Figure 2(c), imaged from the same area shown in Figure 2(b), shows a dark-field micrograph of the D0_3 phase domains. The size of the domains is fairly small and the amount of D0_3 is substantial. The electron diffraction pattern from the same area indicates the presence of the D0_3 , probably mixed with the B2 ordered phase. Figure 2(d) shows, at lower magnification, the uniform APB structure throughout the matrix and occasional dislocations in the as-cast alloy. Very few dislocations were found in the matrix of the as-cast alloy. The dislocations are large compared to the size of the D0_3 domains, and their bowed appearance suggests that they may be pinned by the D0_3 APBs. The very low dislocation content and the finely dispersed D0_3 domain structure may both contribute to the poor ductility observed in the as-cast material. Analytical electron microscopic analysis of rod precipitates and further investigations on the effects of homogenization on precipitate morphology and matrix ordered phase are in progress.

Homogenization Studies

Specimens obtained from the slab mold ingot were homogenized at 1200 and 1300°C for periods ranging from 1 to 32 h, with times being doubled at each step. Optical, scanning electron and transmission electron micrographs were obtained from selected specimens.

In samples homogenized at 1200°C, a gradual change in morphology was observed in the globular interdendritic phase. Particles became larger and fewer during homogenization. Optical micrographs did not indicate a comparable change in the rod-shaped particles. Figure 3(a and b) shows scanning electron micrographs of specimens homogenized at 1200°C for 1 h and 32 h, respectively. Energy dispersive spectroscopy (EDS) analysis of specimens homogenized at 1200°C (Table 2) indicates that the interdendritic phase became richer in niobium during homogenization. At the end of the 32-h homogenization, the particles were almost completely niobium, indicating the likelihood of the particles being niobium carbide. Rod particles did not show a change in composition with homogenization time. However, the size and shape of the rod particles makes accurate microcompositional analysis in the scanning electron microscope (SEM) more difficult due

(a)

(b)

(c)

(d)

Fig. 2. TEM micrographs of as-cast FA-129 alloy showing: (a) rod precipitate, (b) APB structure (in bright-field), (c) antiphase domains (in dark-field), and (d) occasional dislocation and uniform APB structure in the background.

Fig. 3. Results of homogenization studies showing SEM micrographs of specimens homogenized at 1200°C: (a) for 1 h, and (b) for 32 h. (c) Optical micrograph of specimen homogenized at 1300°C for 32 h.

to the contribution from the matrix. Figure 3(c) shows an optical micrograph of a specimen homogenized at 1300°C for 32 h. Homogenization at 1300°C caused immediate dissolution of the interdendritic phase and reprecipitation of large particles at the grain boundary. Rod particles also seemed to partially dissolve, but the effect of homogenization was less dramatic. The results of the homogenization treatments as well as the EDS results seem to point to a difference in chemical composition between the rod and the globular precipitates.

Table 2. Energy dispersive spectroscopy analysis of specimens homogenized at 1200°C (wt %)

	Al	Cr	Nb	Fe
<i>Homogenized 1 h</i>				
Overall analysis	11.96	5.97	0.48	81.59
Interdendritic globule	1.77	1.56	80.39	16.28
Interdendritic globule	4.97	3.03	56.50	35.50
Interdendritic globule	3.31	2.29	69.77	24.63
Interdendritic rod	9.65	5.12	16.49	68.74
Matrix rod	4.79	2.75	63.58	28.88
Matrix rod	5.03	3.27	56.22	35.47
<i>Homogenized 32 h</i>				
Overall analysis	11.03	5.60	1.21	82.16
Interdendritic globule	0.56	0.77	92.65	6.01
Interdendritic globule	0.63	0.79	93.42	5.17
Matrix rod	5.22	3.20	52.87	38.71
Matrix rod	4.12	3.03	58.83	34.02
Very fine precipitates	11.53	5.54	0.74	82.20

Interrupted Solidification Tests

Interrupted solidification tests were carried out in an attempt to determine the origin of second-phase particles. Samples obtained from the slab ingot were melted, cooled to a temperature in the freezing range of the alloy (1477 to 1430°C), and quenched in ice water. In the first test, the sample was melted by heating to 1500°C, cooled to 1470°C, held at 1470°C for 15 min, and quenched in ice water. Figure 4(a) shows an optical micrograph of the sample. The regions between grains denote liquid alloy that was quenched at the end

of the test. Dark streaks in the interdendritic region represent segregation. The fraction solid at 1470°C is approximately 0.8. The second sample was melted by heating to 1500°C, cooled to 1460°C in 12 min, held at 1460°C for 12 in, and quenched in ice water. Figure 4(b) shows a micrograph of the sample. The sample is almost 100% solid at 1460°C. The dark regions are segregated interdendritic liquid pools that were quenched at the end of the test. The features of the interdendritic phase are not resolved at this magnification. Figure 4(c) is an optical micrograph of the sample at high magnification revealing extremely fine rod precipitates. The fineness of the precipitates indicates that rod precipitates are probably formed due to a solid-state transformation. The globular interdendritic phase is precipitated from the last liquid to freeze.

Melting and Casting Studies

Melt-quality assessments of AIMs and VIMs were conducted. The FA-129 alloy slab ingots were cast in air and vacuum and subjected to radiographic inspection. In both cases, untreated, partially rusted iron was charged in order to obtain a "worst-case" scenario. Hydrogen samples were taken from the air-induction melt, but not from the vacuum-induction melt, using a commercially available liquid-metal sampler from LECO, Inc. Samples were sent to LECO for analysis. Table 3 lists hydrogen analysis for the air melt (Heat 14843). Diffusible H₂ refers to hydrogen evolved during solidification. Residual H₂ refers to hydrogen dissolved in the metal. Figure 5(a) is a sketch of the slab mold used. Figures 5(b and c) show reproductions (positives) of the radiographs obtained for the AIMs and VIMs, respectively. The porosity indicated in Fig. 5(b) is due to both hydrogen evolution and solidification shrinkage. The porosity indicated in Fig. 5(c) is primarily due to shrinkage. The results are similar to that obtained in previous studies⁴ and indicate that the presence of hydrogen in the melt could be a problem during air melting of iron-aluminide alloys. Further studies will evaluate the effects of argon purging as a means to control hydrogen.

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Fig. 4. Results of interrupted solidification tests: (a) sample quenched from 1470°C showing primary grains and quenched in liquid alloy between grains, (b) sample quenched from 1460°C showing grains and quenched in interdendritic liquid pools, and (c) fine rod precipitates in the sample in (b).

Table 3. Hydrogen analysis for air-induction melt (Heat 14843)

Sample no.	(ppm)		
	Diffusible H ₂	Residual H ₂	Total H ₂
1	2.00	1.06	3.06
2	2.05	1.40	3.45

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Fig. 5(a) Illustration of slab mold, and positive images of radiographs obtained for (b) an air-induction melt, and (c) vacuum-induction melt. Dark areas in radiographic images denote porosity.

2.6 DEVELOPMENT OF WELDABLE HIGH-STRENGTH IRON ALUMINIDES

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INTRODUCTION

Iron aluminides based on Fe_3Al have excellent oxidation and corrosion resistance.¹ However, until recently their potential use as structural material has been hindered by low room temperature ductility (<5%) and a drop in strength above 600°C.² Development efforts at this laboratory have indicated that by controlling alloy chemistry and thermomechanical processing, the environmental embrittlement, which leads to reduced ambient-temperature ductility in this alloy system,³⁻⁵ can be minimized, and Fe_3Al -based alloys can be produced with ambient temperature tensile ductilities of 10-20% and tensile yield strengths of as high as 500 MPa.^{6,7} However, the tensile strength of Fe_3Al -based alloys decreases dramatically above 600°C.⁷ The high temperature tensile strength can be improved with alloying additions,⁷⁻⁹ but often at the expense of room temperature ductility.

Fe_3Al has also been known for some time to have very poor creep resistance²; at 593°C (1100°F) and 207 MPa (30 ksi), the binary lasts only 2-5 h. Alloying additions, such as niobium and zirconium have extended the creep life to over 300 h.¹⁰ With the addition of other elements, such as chromium, added to increase room-temperature ductility, synergistic effects become important. Some of these effects have been identified.⁸⁻¹² For example, elements such as chromium and molybdenum, which go into solution as ternary additives, will form precipitates when elements such as boron, carbon, zirconium, or niobium are also present.^{2,6,7} These precipitates refine grain size and provide strengthening, particularly at room temperature.

Welding is another major area of concern for realizing the potential benefits of the unique properties of iron aluminides. The welding processes used must be capable of producing high quality weldments under field and shop conditions which are free of cracks and have good mechanical properties in comparison to the base metal. The alloy FA-129 (Fe-28Al-5Cr-0.5Nb-0.2C, at.%) has been found to be weldable by optimizing the welding process and parameters (e.g., using pre- and post-weld heat treatments).¹² Studies have shown that the weldability of iron aluminides is very sensitive to minor changes in the composition of the base metal.^{13,14}

This task was initiated in FY-1992 with the objective of using alloy FA-129 (Fe-28Al-5Cr-0.5Nb-0.2C), which has good weldability, good tensile strength, and acceptable RT tensile

ductility ($>10\%$), and further modifying its composition to produce improved high-temperature creep-rupture and tensile strength. Studies have indicated that the best elements to add for improved strength, without producing significant reductions in RT ductility, are Mo, Nb, and Zr.¹⁰ Alloy FA-97 (Fe-28Al-2Cr-0.5Nb-2Mo-0.1Zr-0.2B) was shown to have excellent creep-rupture properties and RT tensile strength, but very low RT tensile ductility⁷ and poor weldability.¹⁵ Several iterations of alloy compositions between FA-129 and -97 have resulted in alloys which may provide a compromise in properties.¹⁶ The most recent alloy compositions and their creep-rupture and RT tensile properties are listed in Tables I and II, respectively. These studies have suggested that a certain ratio of molybdenum, niobium, and zirconium is desirable for best creep resistance, but too much of any one can harden the alloy and lower the RT tensile ductility. On the other hand, too much zirconium or boron results in reduced weldability, while a little carbon promotes weldability.¹⁵ The properties of the most recent series of alloys (Table II) indicate that (1) levels of 0.03-0.05 at.% C are acceptable for both creep resistance and weldability; (2) boron is not necessary for creep resistance and may not be needed for ductility, but in any case, to promote weldability, should be kept at 0.005% or less; (3) for weldability, the zirconium level should be kept below 0.05%; and (4) the molybdenum level needs to be near or above 0.4% for creep resistance.

More effort will be used in this task to study the kinds and distribution of precipitates produced by alloying additions and selected heat treatments, and the relationships of these precipitates to properties. To accomplish these objectives, more time and funding will be devoted to compositional analysis techniques (e.g., microprobe analysis, x-ray fluorescence) and to transmission electron microscopy (TEM), including analytical electron techniques. In particular, this task will attempt to determine why alloy FA-97 has such good creep-rupture properties, why alloy FA-129 has such poor creep strength but good tensile properties, and how one can use the acquired knowledge to design an alloy composition with the best compromise

Table I. Compositions of iron aluminides under study								
Alloy Designation	Nominal composition (at.%)							
	Al	Cr	Nb	Mo	Zr	C	B	Fe
FA-97	28	2.0	0.5	2.0	0.1		0.2	Bal.
FA-129	28	5.0	0.5			0.2		Bal.
FA-167	28	5.0	0.5	0.25	0.025	0.1	0.005	Bal.
FA-168	28	5.0	0.5	0.8	0.05	0.03	0.005	Bal.
FA-169	28	5.0	0.5	0.25	0.025	0.05		Bal.
FA-170	28	5.0	0.5	0.4	0.025	0.05		Bal.

Table II. Properties of Fe ₃ Al alloys							
Alloy	RT Tensile ^{a,b}			Creep rupture ^c			Sigmajig TCS ^d (MPa)
	Yield (MPa)	Ultimate (MPa)	Elong. (%)	Life (h)	Elong. (%)	MCR (%/h)	
FA-129	357 ^{e,f}	779	11.0	22 ^{e,g}	75	0.95	=172
FA-97	454 ^{e,g}	520	1.2	463 ^{e,g}	47	0.04	<<138
FA-97				750 ^{f,h}	35	0.03	
FA-167	505(509) ^{e,f}	723(822)	5.4(8.6)	84 ^{e,f}	47	0.3	=138
FA-168	635(686) ^{e,f}	744(773)	2.5(4.9)	391 ^{e,f}	65	0.06	<<138
FA-169	(502) ^{e,f}	(803)	(8.7)	40 ^{f,h}	36	0.6	<103
FA-170	(474) ^{e,f}	(680)	(5.5)	281 ^{f,h}	32	0.04	103-138
^a Values in parentheses were produced using grips designed to hold the specimen under the shoulders, not in the pinholes. ^b Tensile tests conducted in air at a strain rate of 3.3×10^{-3} /sec. ^c Creep-rupture tests conducted at 593°C and 207 MPa. ^d TCS = Threshold cracking stress. ^e Hot rolled at 600°C. ^f Heat treatment 1h/750°C, air cooled. ^g Heat treatment 1h/850°C+3-7d/500°C. ^h Hot rolled at 850°C; starting microstructure consisted of larger recrystallized grains.							

of tensile and creep properties. Crack-free welds are also desired, and elements which tend to produce good welds will also be favored. This work is being coordinated with related efforts sponsored by the Advanced Industrial Concepts Materials Program.

RESULTS AND DISCUSSION

All Fe₃Al alloys for this study were prepared by arc-melting and drop-casting into chilled copper molds. Hot rolling to 0.76-mm-thick sheet was accomplished by various rolling and forging steps beginning at 1000°C and ending at either 850 or 600°C. Flat tensile specimens (0.76 × 3.18 × 12.7 mm) were mechanically punched from the hot-rolled sheet. Specimens were annealed for 1 h at 850°C, followed by 3-7 d at 500°C, or for 1 h at 750°C. Tensile tests were conducted at room temperature (RT) and at 600°C in air at a strain rate of 3.3×10^{-3} s⁻¹. Creep-rupture tests were conducted in air at 593°C and 207 MPa. Data values reported are averages of at least two tests. Optical metallography, scanning (SEM), transmission (TEM), and analytical electron microscopy (AEM) were used to study microstructures.

The sensitivity to fusion zone cracking was established using the Sigmajig weldability test.¹⁷ The test uses a pre-applied transverse stress during the autogenous gas tungsten arc welding of a 50 mm by 50 mm sheet specimen. The applied stress is sequentially increased until the specimen cracks. This test ranks materials based on the threshold cracking stress (TCS) above which cracking in the fusion zone occurs.

After a consideration of the properties of alloys listed in Table I, alloy FA-170 (Fe-28Al-5Cr-0.5Nb-0.4Mo-0.025Zr-0.05C) was chosen for further studies under this new task. Table III shows the results of creep-rupture tests at 593°C and RT tensile tests on alloy FA-170 using three different fabrication schedules. Heat #14432 was air-melted into a 2-kg rectangular ingot, cut in half, and fabricated using two different rolling schedules:

- (1) Clad in carbon steel, anneal 2 h at 1150-1200°C to homogenize; hot-roll at 1000°C to 2.5 mm, 25%/pass; remove cladding and anneal 1 h at 1100°C to recrystallize; hot-roll at 850°C to 0.76 mm, 10-15%/pass, with 1 h at 1100°C every three passes, end with 10-20% cold work.
- (2) Clad in carbon steel, anneal 2 h at 1000°C; hot-roll at 1000°C to 7.5 mm, 25%/pass; hot-roll at 850°C to 2.5 mm, 25%/pass; remove cladding and anneal 1 h at 1000°C to recrystallize; hot-roll at 650°C to 1.75 mm, 15%/pass; anneal 1 h at 750°C to stress-relieve; hot-roll at 600°C to 0.76 mm, 10%/pass.

The microstructure produced by fabrication schedule #(1) consisted of large recrystallized grains (approximately 200 μm diam), and produced excellent creep-rupture properties (see Table III). On the other hand, schedule #(2) produced a much smaller grain size (25-50 μm), which resulted in lower creep life and better RT tensile properties. These results indicate that the mechanical properties are strongly dependent on the microstructures produced during fabrication.

Heats #14834 and #14834R were melted by vacuum induction into 7-kg round ingots and fabricated according to the following schedule:

- (3) Hot-extrude at 1000°C from 72 round to 44 × 25 mm rectangular bar (72.5% area reduction); cut into 152-mm-long pieces; hot forge at 800°C to 13-mm thickness; hot-roll at 800°C to 6.4 mm; hot-roll at 650°C to 0.76-mm sheet.

Heat #14834 exhibited poor creep properties (see Table III) and, although RT tensile properties were better than for heat #14432, the tensile data contained a lot of scatter. The use of various heat treatments to control the microstructure did not result in significant

Table III. Test history of alloy FA-170							
Heat # Fab. #	Heat Treat- ment ^c	Creep-rupture tests ^a			RT tensile tests ^b		
		Life (h)	Elong. (%)	MCR (%/h)	Yield (MPa)	Ultimate (MPa)	Elong. (%)
14432 (1)	A	281.1	32.5	0.04	304		<1.0
	A	270.9	39.9	0.04	295	316	1.3
14432 (2)	A	42.7	41.7	0.6	457	510	1.5
	A	39.5	59.4	0.6	474	680	5.5
	A	107.0	39.5	0.15			
14834 (3)	A	10.5	80.0	2.2	478	883	7.6
	A	10.2	86.2	2.4	483	825	6.1
	A				467	854	7.5
	A				508	905	11.8
	B				528	937	11.1
	B				509	1011	15.5
	C	7.2	64.0	5.0			
	D	25.9	22.2	0.09			
	D	24.9	16.1	0.07			
	E	4.2	11.4	0.3			
	AP	13.0	61.9	1.8			
14834R (3)	A	31.1	79.4	0.85	550	925	11.0
	A	35.55	78.4	0.77	547	936	11.5
	F	71.15	60.3	0.3			
	F	51.5	53.5	0.4			
	D	53.4	42.8	0.43			
	D	41.5	38.3	0.47			
^a Creep-rupture tests conducted at 593°C and 207 MPa. ^b Tensile tests conducted in air at a strain rate of 3.3×10^{-3} /sec. ^c Sheet was annealed 1 h at 700°C before specimens were punched and specimens were annealed before testing using these heat treatments. A=1h/750°C air cooled; B=1h/750°C oil quenched; C=1h/850°C; D=1h/1200°C; E=17h/1225°C; F=1h/1000°C; AP=as punched.							

improvement in the creep properties (see Table III). Subsequent chemical analysis indicated that heat #14834 was low in aluminum (26% instead of 28%). A new heat (#14834R), which was determined to be very near the nominal composition, produced better creep properties, as well as better RT tensile properties. However, the creep-rupture properties are not yet as good

as expected for this composition. The effects of fabrication techniques and microstructure on the creep-rupture properties of this alloy will continue to be studied.

Figure 1 shows typical TEM microstructures of FA-129 and FA-97 creep-ruptured to failure at 593°C and 207 MPa. The microstructure of FA-129 had few precipitates, but a well-defined network of anti-phase boundaries which were identified as the B2 phase. Although dislocations appeared to be generated at some grain boundaries [Fig. 1(a)], the absence of profuse dislocation networks suggested that, in this alloy, dislocation generation and recovery occurred at about the same rates. The microstructure is consistent with a composition which does not work-harden, but instead is very weak in creep (this specimen lasted ~20 h, with a minimum creep rate of about 1%/h), with a short secondary stage and rapid initiation of tertiary creep leading to failure. In contrast, the microstructure of FA-97 was dominated by dislocation networks and fine background loops, indicative of an alloy which resists failure (this specimen lasted over 460 h, with a minimum creep rate of 0.04%/h).

The alloys listed in Table I were tested for hot-crack susceptibility using the Sigmajig test. The results, presented in the last column of Table II, clearly show that the weldability of iron aluminides are sensitive to changes in composition. The high TCS value for alloy FA-129 indicates that it has a high potential for good weldability. Among alloys FA-167 to -170, all except alloy FA-168 exhibited promise of good weldability, the main difference between the alloys being the higher molybdenum and zirconium content in FA-168. Sigmajig tests of heat #14834 (which was low in aluminum) of composition FA-170 produced one of the best TCS values so far measured (186 MPa); values for heat #14834R are yet to be measured.

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Figure 1. TEM microstructures of (a) FA-129 and (b,c) FA-97 creep-ruptured to failure at 593°C and 207 MPa.

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2.7 ENVIRONMENTAL EFFECTS ON IRON ALUMINIDES

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INTRODUCTION

Iron aluminide alloys containing aluminum concentrations in the range of 16 to 28 at. % aluminum and 0 to 5 at. % chromium were fabricated into corrosion coupons and tested in $\text{H}_2\text{S-H}_2\text{-H}_2\text{O}$ gas mixtures at 800°C and in air at 900 to 1000°C . Similar tests were conducted on developmental Fe-Cr-Al alloys supplied by Harwell Laboratory (UK). Effects of zirconium additions on scaling resistance in air were also evaluated based on the comparative performance of alloys containing 28% Al, 0 to 5% Cr, and 0 to 0.1% Zr. The critical aluminum content required to sustain sulfidation resistance in $\text{H}_2\text{S-H}_2\text{-H}_2\text{O}$ was found to be on the order of 18 at. %. However, all of the Fe-Al alloys were much more resistant to the $\text{H}_2\text{S-H}_2\text{-H}_2\text{O}$ gas mixture than the Fe-Cr-Al alloys under equivalent conditions. A 20% Al level was found to be critical for sustained oxidation resistance of binary Fe-Al alloys in air at 900°C or above. Air tests of the Fe-Cr-Al class of alloys at 800 and 900°C gave oxidation rates comparable to Fe_3Al -based alloys. In the case of alloys containing 28% Al, additions of zirconium significantly improved the spalling resistance in air above 900°C .

Iron-based alloys containing 28 to 40 at. % Al have been under development for potential applications in coal gasifiers and fossil fuel-fired boilers.¹ These alloys exhibit exceptional resistance to sulfidizing atmospheres containing $\text{H}_2\text{S-H}_2\text{-H}_2\text{O}$ or SO_2 , as well as to oxidizing atmospheres such as air or molten salts.² Further investigations of the corrosion performance of the alloys have been made to examine the effects of compositional modifications, specifically the critical concentrations of aluminum required for resistance to sulfidizing and oxidizing environments as a function of temperature and third-element alloying additions. The corrosion resistance of Fe-Al alloys containing 16 to 22 at. % Al, developed under a companion Advanced Research and Technology Development (AR&TD) program,³ were evaluated relative to the Fe_3Al alloys (28% Al). Similar tests were conducted on Fe-Cr-Al alloys nominally containing 20 at. % Cr and 10 at. % Al, which

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are under development at Harwell Laboratory (UK). To simulate gasifier environmental conditions, alloys were exposed to H₂-Ar mixtures containing controlled amounts of H₂O and H₂S, and to simulate combustion conditions, exposures were conducted in an air atmosphere.

Experimental Procedures

The alloys evaluated in this study were obtained from two sources. Compositions listed in Table 1 (developmental Fe-Cr-Al alloys) were supplied by Harwell Laboratory in the form of 3.2-mm plate, which was subsequently cold rolled at Oak Ridge National Laboratory (ORNL) to a thickness of 1.6 mm. Binary Fe-Al alloys and alloys based on Fe₃Al 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 cold rolled to plate of 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 sectioned from the plate and mechanically abraded on the two major surfaces, ending with 600-grit abrasive. Corrosion resistance of the specimens was determined by weight change measurements using Cahn 1000 continuously recording microbalances. The test environment was composed of either a 5.45% H₂S-79.4% H₂-1.64% H₂O-13.6% Ar (by volume) gas mixture or laboratory (dry) air and was replenished at a rate of 110 cc/min. Temperatures relating to gasifier applications ranged from 500 to 800°C, while those for combustion applications extended to 1000°C. Tests were normally conducted for 1 week (168 h), after which the specimens were visually and metallographically examined. Selected specimens were also tested under thermal cycling conditions in ambient air in horizontal tube furnaces, the specimens being removed from the furnace and weighed every 24 to 72 h.

Table 1. Compositions of Fe-Cr-Al alloys supplied by Harwell Laboratory (at. %)

Alloy	C	Si	Mn	Cr	Ni	Al
VB 1852	0.074	0.41	0.38	20.3	0.24	9.11
VB 1901	0.060	1.64	0.53	21.4	0.07	10.1
VB 1902	0.085	4.09	0.53	21.7	0.08	9.47

Results

Tests in H_2S - H_2 - H_2O -Ar

Fe-Al alloys with aluminum concentrations ranging from 16 to 22 at. % were exposed to the reference H_2S - H_2 - H_2O -Ar gas mixture for one week at 800°C . As shown in Fig. 1, the resultant weight changes were relatively small for binary alloys containing $\geq 18\%$ Al but increased sharply when the concentration dropped to 16%. Adding 5% Cr to the alloys decreased the corrosion rate at the 16% Al level but increased the rate at the 22% level (Fig. 2). In Fig. 3 it can be seen that the weight change behavior of the 22% Al alloy was essentially the same as that of a 28% Al alloy (Fe_3Al), and the effect of chromium at the respective aluminum levels was also similar.

Fig. 1. Effect of aluminum content on corrosion rates of Fe-Al binary alloys in mixed gas.

Fig. 2. Effect of 5% Cr additions on corrosion of Fe-16%Al and Fe-22%Al in mixed gas.

Under the same test conditions, Fe-Cr-Al alloys containing 20 to 22 at. % Cr and 9 to 10 at.% Al (Table 1) showed much higher weight gains than even the Fe-16% Al composition noted above. Figure 4 compares the corrosion rates of three of the former compositions with Fe-16%Al-5%Cr over a 24-h period. An alloy containing 4 at. % Si showed a slightly lower weight gain than the other two Fe-Cr-Al compositions.

Fig. 3. Comparison of corrosion rates of Fe-22%Al binary and 5% Cr compositions with Fe₃Al alloys in mixed gas.

Fig. 4. Corrosion rates of Fe-Cr-Al alloys (20%Cr-10%Al) compared with Fe-16%Al-5%Cr in mixed gas.

Tests in Air

The effect of aluminum concentration on resistance to air oxidation of binary Fe-Al alloys at 900°C is shown in Fig. 5. In this case, the critical aluminum concentration required to sustain relatively low corrosion rates appeared to be above 18 and nearer 19.5 at. %. Again, there was no further improvement in oxidation resistance for aluminum concentrations over 19.5%. The addition of 5% Cr to the alloys reduced the weight gain at an aluminum concentration of 16% but had no measurable effect on oxidation rate at 22% Al (Fig. 6). The beneficial effect of chromium at lower aluminum concentrations was also borne out in air oxidation results for the developmental Fe-Cr-Al alloys listed in Table 1. As shown in Fig. 7, the oxidation rates of the latter alloys (except for the alloy containing 4 at. % Si) at 900°C were comparable to that of an Fe₃Al-based alloy, and comparison of Figs. 5, 6, and 7 shows that the rates for the Fe-Cr-Al alloys were lower than for binary Fe-Al alloys containing less than 19.5% Al and for a 16% Al alloy containing 5% Cr.

Oxidation studies of Fe₃Al-based alloys at 900 and 1000°C have shown a significant effect of zirconium on the spalling resistance of the alloys in air. Figure 8 records the weight changes of Fe-28% Al, Fe-28% Al, 5% Cr, 0.1% Nb, 0.16%C, and Fe-28% Fe-28% Al, 5% Cr, 0.1% Zr, 0.05%B specimens that were exposed at 1000°C and air cooled to room temperature every 24 to 72 h for a duration of 700 h. The former two alloys lost weight continuously during the test and exhibited oxide spalling on cooling, while the latter

Fig. 5. Effect of aluminum content on corrosion rates of Fe-Al binary alloys in air.

Fig. 6. Effect of 5% chromium additions on corrosion of Fe-16%Al and Fe-22 % Al in air.

Fig. 7. Corrosion rates of Fe-Cr-Al alloys (20%Cr-10%Al) compared with Fe_3Al (Fe-28%Al) in air.

Fig. 8. Weight changes of Fe_3Al -based alloys under thermal cycling condition in air at 1000°C.

relatively small weight gain with no evidence of oxide spalling. Five separate thermal cycling experiments at 1000°C and one at 900°C yielded similar results-the alloys without zirconium lost weight because of spallation, while the alloy with 0.1% Zr monotonically gained weight. The effect of zirconium was confirmed by similar cyclic oxidation experiments where two Fe₃Al alloys (Fe-28%Al-4%Cr and Fe-28%Al-4%Cr-0.1%Zr) differed only with respect to zirconium. The zirconium-containing alloy again showed better spalling resistance in tests at 900°C. Depth profiling and scanning Auger analysis of the scale formed on the latter specimen showed the scale to contain only aluminum and oxygen with no detectable zirconium.

DISCUSSION

Test results for Fe-Al alloys in a mixed gas containing H₂S indicate that the 28% Al concentration specified for currently adopted Fe₃Al compositions is several percent higher than the minimum needed to suppress sulfidation at 800°C. Corrosion rates for binary alloys containing from 18 to 22% Al were similar to those of a binary alloy containing 28% Al and were actually lower than for Fe₃Al alloys containing 4 to 5% Cr. However, an aluminum concentration higher than the required threshold is obviously desirable to avoid selective depletion of this element in longer term corrosion applications, particularly where scale spalling occurs.

Although corrosion rates increase significantly when the aluminum concentration is lowered to 16%, they are still markedly lower than those for the Fe-Cr-Al class of alloys, nominally containing 20 at. % Cr and 10 at.% Al. Obviously, chromium is a much less effective addition than aluminum in providing sulfidation resistance against H₂S, as was demonstrated in an earlier study of the sulfidation/oxidation properties of iron-based alloys.⁴ However, at the 16% Al level, slightly below the threshold concentration needed to achieve the optimum resistance to sulfidation, a chromium addition of 5% did serve to improve the corrosion resistance. This effect is unique to the 16% Al level, since a similar chromium addition adversely affects sulfidation in alloys containing 22 to 28% Al. Apparently, at this aluminum concentration, the beneficial effect of chromium in establishing a protective alumina scale⁵ outweighs the negative effect of chromium in promoting the growth of non-protective sulfide reaction products.

In air at 900°C, the threshold aluminum level needed to achieve oxidation resistance on a par with Fe₃Al is near 19.5%. This is slightly higher than that noted above for mixed

gases at 800°C (nearer 18% Al). As was the case for tests in mixed gases, a 5% Cr addition improved the corrosion resistance in 900°C air below the threshold aluminum level, but did not change, or slightly increased, the rate at higher aluminum levels. Unlike the case in mixed gases, oxidation rates for Fe-Cr-Al alloys in air were generally comparable to those of Fe-Al alloys containing aluminum concentrations above the threshold (19.5 to 28% Al). (One exception was a developmental Fe-Cr-Al alloy containing 4% Si, which showed a significantly higher rate of oxidation.) Thus, as has been characteristically observed for air exposures of alloys containing ≤ 10 at. % Al (Ref. 5), chromium plays an essential role at lower aluminum levels in promoting the growth of stable alumina scales. At higher aluminum concentrations, chromium acts to accelerate the earlier stages of oxidation but does not substantially change the longer term (steady-state) oxidation rate.⁶

Although the oxidation rate constants for Fe₃Al-based alloys in air are relatively small, the scales formed at 900°C and above are subject to spallation on thermal cycling. In thermal cycling tests at maximum temperatures of 900 and 1000°C, an Fe₃Al alloy containing 0.1% Zr showed no evidence of oxide spalling over a 700 h period, while two other alloys without zirconium exhibited small weight losses attributable to spalling. The beneficial effect of zirconium on oxide spallation has also been seen in other investigations of alumina-forming alloys.^{7,8} The mechanism by which zirconium improves the scale adherence is uncertain. No accumulation of zirconium was detected by Auger analysis either within the scale or at the scale-metal interface.

Conclusions

Oxidation/sulfidation tests have been conducted on Fe-Al alloys to evaluate the effect of aluminum concentration on corrosion properties. Tests at 800°C in H₂S-H₂-H₂O-Ar mixed gas showed the aluminum concentration needed for optimum sulfidation resistance to be on the order of 18 at. %. Above this concentration, corrosion rates were comparable to those of Fe₃Al-based alloys. However, even at 16% Al, the resistance of binary Fe-Al alloys was markedly superior to that of Fe-Cr-Al alloys nominally containing 20 at. % Cr and 10 at. % Al.

In air at 900°C, the minimum aluminum concentration to achieve optimum oxidation resistance was nearer 20 at. %. Although an addition of 5% Cr improved the oxidation resistance of an alloy containing 16% Al, the corrosion rate was still higher than that of

Fe-Cr-Al alloys with lower aluminum and higher chromium levels. Oxidation rates of the latter alloys in air at 800 and 900°C were comparable to those of Fe₃Al-based alloys.

An Fe₃Al-based alloy containing 0.1% Zr exhibited much better resistance to oxide spalling than alloys without zirconium. The zirconium-containing alloy showed no evidence of scale loss on cooling to room temperature from 900 or 1000°C, while the alloys without zirconium showed slight but repeated scale spallation.

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2.8 DEVELOPMENT OF Cr_2Nb ALLOYS FOR HIGH TEMPERATURE APPLICATIONS

C. T. Liu

INTRODUCTION

The current effort on the development of Cr_2Nb -base alloys is focused on a two-phase microstructure containing patches of the chromium-rich phase embedded in the eutectic matrix [$\text{Cr}_2\text{Nb} + \text{Cr}(\text{Nb})$]. Several high-purity $\text{Cr}_2\text{Nb}/\text{Cr}(\text{Nb})$ alloys were successfully prepared in a high-vacuum arc-melt furnace and cast into a preheated copper mold. This resulted in a reduction in cast porosities and microcracks in the alloys. Fine Nb_2Cr particles ($<1 \text{ mm}$) precipitate out of the chromium-rich solid solution when heat treated at temperatures between 900 and 1200°C for 3 to 5 days. The coarsening of the precipitates at 1200°C reduces the microhardness from 649 to 502 DPH. No microcracks were observed around indents made at a load of 500 g, indicating that the alloy is able to take plastic deformation without cracking.

The objective of this task is to develop new-generation high-strength, corrosion-resistant intermetallic alloys based on Cr_2Nb for use as hot components in advanced fossil energy conversion systems. The intermetallic alloy, Cr_2Nb , with a C-15 cubic structure¹ is attractive for high-temperature structural applications 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 The intermetallic alloy also has a wide range of compositional homogeneity,³ suggesting the possibility of improving its mechanical and metallurgical properties by alloying additions.

The major concern with this intermetallic alloy is its poor ductility and fracture toughness at ambient temperatures.^{2,5} The single-phase Cr_2Nb is very hard ($\sim 800 \text{ DPH}$) and extremely brittle at room temperature. Previous studies indicated that the mechanical properties of Cr_2Nb could be improved by introducing chromium-rich particles through a precipitation reaction. Some two-phase alloys exhibited a compressive ductility of 4% at room temperature and a yield strength of over 700 MPa ($\sim 100 \text{ ksi}$) at 1000°C. These intermetallic alloys were substantially stronger than existing nickel-base superalloys at temperatures at least to 1250°C and offer strengths equivalent to some structural ceramics

at these temperatures.⁵ The mechanical properties of Cr₂Nb/Cr(Nb) alloys were further improved by some alloying additions.⁶

Limited results obtained previously indicate the excellent strength of Cr₂Nb/Cr(Nb) alloys for structural use at ultra-high temperatures (e.g., 1000-1300°C).⁵ Potential applications include critical hot components in advanced coal conversion systems, advanced heat engines, and high-temperature cutting and grinding tools. The alloys, on the other hand, exhibited no tensile ductility at ambient temperatures. They showed some oxidation resistance at elevated temperatures, but long-term exposures at 1000°C resulted in the spalling of oxide scales from surfaces.⁶ This paper summarizes our recent alloy development effort on improving the mechanical and metallurgical properties of some Cr₂Nb/Cr(Nb) alloys. A detailed study of the corrosion behavior of similar alloys is reported in the paper, "High-Temperature Oxidation of Cr-Cr₂Nb Alloys," by Tortorelli and DeVan in these proceedings.⁷

Material Preparation

The alloy development effort was started by preparation of high-purity Cr₂Nb/Cr(Nb) alloys with minimum cast defects. The mechanical properties of brittle materials are generally sensitive to interstitials (such as oxygen and nitrogen), and it is thus important to keep the interstitial contents as low as possible in these alloys. To achieve this goal, high-purity niobium (containing <200-wt ppm oxygen) and chromium metal chips were used, and the alloys were prepared in a high vacuum system to avoid interstitial contamination. Our existing melting and casting equipment was modified in order to achieve a high vacuum of 10⁻⁵ Pa (~ 10⁻⁷ torr). Cast molds were designed to be preheated to as high as 500°C for control of alloy solidification and microporosity formation during drop casting.

At present, seven high-purity ingots containing 12 at. % Nb and other alloying elements were prepared by arc melting and drop casting in the upgraded processing equipment. The cast mold was preheated to 250-350°C prior to alloy casting. Four alloy ingots, CN-43, -49, -50, and -51, showed no macrocracks, whereas three ingots, CN-46, -47, and -48, exhibited a few macrocracks visible on ingot surfaces. This observation indicates that the cracking behavior is sensitive to alloy composition. The alloy ingot CN-43 was sectioned for metallographical examination, which showed no indication of microcracks in this ingot. Some fine porosity was observed; however, the size and numbers of pores are

much less as compared with those in the ingot with the same composition prepared previously.^{5,6}

Heat Treatment and Microstructural Analysis

The alloy CN-43 basically contains two phases, i.e. the Cr_2Nb intermetallic phase and the chromium-rich solid solution containing up to 6% Nb.⁵ To control the two-phase microstructure, CN-43 samples were first annealed for five days at 900°C, followed by re-annealing for three days at 1000°C, 1100°C, or 1200°C in evaluated capsules. Figure 1 shows the optical microstructure of the as-cast and annealed CN-43 samples. In the as-cast condition, the alloy exhibits patches of the chromium-rich phase surrounded by the eutectic matrix [Fig. 1(a)] containing Cr_2Nb and chromium-rich phases. The alloy is basically free from microcracks and cast defects. The chromium-rich patches started to precipitate out fine Cr_2Nb particles when being annealed for five days at 900°C, and the particles apparently are too small to be resolved clearly at a magnification of 650X [Fig. 1(b)]. The precipitates coarsened during annealing at 1000-1200°C for three days, and individual particles are clearly visible in the sample annealed at 1200°C [Fig. 1(d)].

Fig. 1 Optical micrograph of CN-43 samples (a) as-cast, (b) annealed 5 d/900°C, (c) annealed 5 d/900°C+3 d/1100°C, and (d) annealed 5 d/900°C+3 d/1200°C; 625X.

The composition of the phases was determined by electron microprobe analyses. Figure 2 shows the backscattered electron image of as-cast and 1200°C-annealed samples. In this case, the phase with a dark gray contrast is the chromium-rich solid solution and the phase with a bright contrast is the Cr_2Nb -type phase. There was no indication of precipitates in the chromium-rich patches in the as-cast sample, [Fig. 2(a)], while individual precipitates were clearly visible in the chromium-rich patches in the sample annealed 5-d/900°C plus 3-d/1200°C [Fig. 2(b)]. Cr_2Nb precipitates were extremely fine, less than 1 mm in size, even after annealing for 3-d at 1200°C. This indicates a slow diffusion and high stability of the Cr_2Nb phase in the alloy. The chromium-rich patches formed during solidification contain as much as 6-at.-% Nb, as determined by wavelength-dispersive spectrometry (WDS) analyses. This is consistent with the solubility limit of niobium in the chromium-rich phase reported previously.⁵ The partitioning of alloying elements in the chromium-rich and Cr_2Nb phases was also carefully determined by the WDS analyses.

Fig. 2 Backscattered electron image of CN-43 samples. (a) As-cast, and (b) annealed 5 d/900°C+3 d/1200°C; 660X.

A few foreign particles with a dark contrast were observed in the as-cast and annealed samples. Spot analyses using WDS indicated that they were mainly aluminum oxide particles. No carbon was detected in these particles.

Mechanical Properties

The determination of mechanical properties of CN-43 was limited to microhardness measurements. Table 1 shows the hardness of CN-43 as a function of heat treatment.

Table 1. Effect of heat treatment on microhardness of CN-43 Alloy

<u>Heat Treatment</u>	<u>Hardness (DPH)</u>
As-cast	649±15
5 d/950°C	638±5
5 d/900°C+3 d/1000°C	570±10
5 d/900°C+3 d/1100°C	562±11
5 d/900°C+3 d/1200°C	502±13

Each data point reported here represents an average of three measurements. The as-cast and 900°C/5-d annealed samples exhibited the highest hardness (638-649 DPH). Cr₂Nb precipitation at 1000 and 1100°C reduced the hardness to 562-570 DPH. Consistent with the hardness, these two annealed samples showed almost identical microstructure, that is, no apparent difference in growth of Cr₂Nb precipitates in the chromium-rich patches at 1000°C and 1100°C. Coarsening of Cr₂Nb precipitates at 1200°C caused a drop of hardness to 502-DPH. It is important to point out that no cracks were observed around indents at a load of 500 g in all CN-43 samples (Fig. 3). This indicates that the alloy is able to accommodate plastic deformation without cracking.

The tensile and creep properties of the alloy CN-43 will be measured on button-type specimens prepared by electro-discharge machining. Specimen preparation and mechanical testing are in progress.

Summary and Future Work

High-purity alloy ingots based on Cr₂Nb were prepared in a modified processing apparatus in a high vacuum of 10⁻⁵ Pa. The cast mold was designed to be able to preheat to 250-350°C for minimizing cast defects (such as microcracks). The alloy CN-43 basically contains two phases: the Cr₂Nb intermetallic phase and the chromium-rich solid solution containing up to 6 at % Nb in the as-cast ingot. The heat treatment at 900-1200°C caused precipitation of Cr₂Nb-type precipitates in the chromium-rich primary patches. The particles

Fig. 3 No microcracks formed around an indent in the CN-43 sample annealed for 5d/900°C+3d/1200°C.

are very stable and show no significant particle growth at temperatures at or below 1100°C. The annealing at 1200°C for 3 days coarsens Cr_2Nb precipitates to 1- μm in diameter and reduces the microhardness from 649 to 502 DPH. No cracks were observed around indents made at a load of 500g.

Further studies will include the preparation of tensile specimens by electro-discharge machining. The tensile and creep properties will be measured as a function of temperature and applied stress. The mechanisms governing crack nucleation and growth will be identified by carefully examining deformed and fractured specimens. This study is expected to lead to the establishment of a structure/property correlation for alloy design.

The chromium-rich phase is much tougher than the brittle Cr_2Nb phase; however, it is not sufficiently ductile when deformed in tension.⁵ Our alloy development effort will be devoted to increasing the ductility and toughness of the chromium-rich phase by alloy additions. For this purpose, a group of alloying elements will be added to $\text{Cr}_2\text{Nb/Cr(Nb)}$ alloys at different levels. The selection of the alloying elements will be based on consideration of both physical-metallurgy principles and empirical relationships. The partitioning of these elements in the matrix and particles will be characterized by various microanalytical tools. This effort is expected to result in development of two-phase intermetallic alloys with improved toughness and ductility at ambient temperatures and with excellent strength at elevated temperatures for structural use.

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2.9 HIGH-TEMPERATURE OXIDATION OF Cr-Cr₂Nb ALLOYS

P. F. Tortorelli and J. H. DeVan

INTRODUCTION

The high-temperature oxidation of Cr-Cr₂Nb alloys is being studied as part of a program to develop ductile, corrosion-resistant versions of this very-high-strength material. The kinetics, scale development, and spallation tendencies of Cr -6 and -12 at. % Nb alloys oxidized in air at 900 and 950°C were characterized. The alloy with the higher niobium content performed significantly better in terms of overall weight gain and resistance to spallation. This behavior is ascribed to an increased volume fraction of the Cr₂Nb-Cr eutectic mixture at the expense of the Cr-rich phase. The study suggested some general approaches to improving the oxidation resistance of Cr-Nb alloys.

At present, any advances in operating temperatures and, hence, thermal efficiencies of heat engines and energy systems are limited by strength or corrosion considerations. There is thus a pressing need to develop new materials (particularly metallic ones) that can be used in hostile environments at elevated temperatures. Laves-phase alloys based on Cr₂Nb may offer a possible solution to the materials problems associated with such high temperature deployment. In compression, Cr-Cr₂Nb alloys have been shown to be substantially stronger than conventional nickel-based superalloys at high-temperature while exhibiting some ductility.¹ However, much more development is needed to overcome poor ambient temperature ductility and low fracture toughness. In addition, there is some concern regarding the corrosion resistance of Cr-Nb intermetallic alloys in the temperature range of interest. It is therefore important to evaluate the scaling of such alloys in terms of whether the surface products that form provide the necessary corrosion resistance under a variety of environmental conditions.

To be corrosion resistant at high temperatures, alloys must form surface reaction products that protect the underlying metal from environmental degradation. In order to do this, the product(s) must grow relatively slowly, provide a sound barrier that prevents direct interaction between the environment and alloy, and remain adherent to the metallic substrate. In many technologically important cases, chromia scales meet some or all of these requirements and, therefore, the oxidation of chromium and chromium-containing alloys has been studied

requirements and, therefore, the oxidation of chromium and chromium-containing alloys has been studied extensively. (A good summary can be found in ref. 2.) However, the protection afforded by adherent chromia is limited by evaporation of CrO_3 which, at sufficiently high temperatures, forms by oxidation of Cr_2O_3 :

This reaction typically becomes important at 1100 to 1200°C and serves to place an upper limit on the use of alloys protected by chromia scales.

Oxides of niobium are thermodynamically more stable than Cr_2O_3 , (refs. 3,4) but they are not necessarily protective. Typically, Nb_2O_5 scales are porous²⁵ and offer little oxidation resistance. On the other hand, NbO and NbO_2 are normally protective in oxidizing environments when they are the predominant oxide species.⁵ The present work represents the initial effort toward establishing the nature of the oxides that grow on Cr-Nb alloys at high temperatures; evaluating their protectiveness in terms of growth kinetics, scale integrity, and adherence; and determining the optimal metallurgical and environmental conditions for corrosion resistance. Specifically, results on oxidation kinetics and scale spallation, morphology, and composition are reported for air exposures of Cr -6 at. % Nb and -12 at. % Nb alloys at 900 and 950°C. (Such temperatures represent the lower end of the anticipated operating range for such alloys.)

Experimental Procedures

Two alloys with nominal compositions of Cr-6Nb and Cr-12Nb (at. %) were prepared by arc melting and drop casting into water-cooled copper molds. As-cast 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 abrasive before exposure.

Weight change behavior was characterized using Cahn 1000 microbalances and a computer-controlled data acquisition system. The specimens were isothermally exposed to flowing, preheated, dried air (110 cc/min) at 900 and 950°C for up to 180 h. At the end of each exposure, the furnace was immediately removed from around the reaction tube, and the monitoring of weight change was continued until the specimen had cooled to below 200°C.

Following exposure, the coupons were visually checked for evidence of loss of corrosion products by spallation. The specimens were then analyzed by scanning electron

microscopy (SEM) with associated energy-dispersive X-ray (EDX) analysis. In one case, a polished cross section was examined using optical imaging.

Results

The 950°C thermogravimetric data for the -6 and -12Nb specimens are shown in Fig. 1. Note that the specimen with the higher niobium concentration exhibited lower weight gains during exposure at 950°C and smaller losses upon cooldown. Results of visual examination of the scales (summarized in Table 1) confirmed that there was very little spallation for Cr-12Nb (mostly around the edges), while a substantial fraction of the exposed surfaces of Cr-6Nb suffered scale loss. A similar effect of niobium concentration was found at 900°C: the -6Nb specimen showed extensive spallation during cooling, while the scale grown on the -12Nb alloy remained almost wholly attached to the substrate (see Table 1). The microbalance data for the 900°C exposures shown in Fig. 2 demonstrated that, as in the 950°C case, larger weight gains were measured for the specimen with the lower niobium concentration. As can be seen in both Figs. 1 and 2, the thermogravimetric curves did not always change smoothly with time. Abrupt increases in weight were recorded at different intervals. Between such events, parabolic behavior was generally observed, that is,

$$w^2 = k_p t, \quad (2)$$

where w is the change in weight per unit surface area, k_p is the parabolic rate constant, and t is time.

SEM revealed similar surface morphologies for the Cr-12Nb specimens oxidized at 900 and 950°C. As shown in Fig. 3, the surfaces were microscopically rough, and there was some evidence of cracking (although it was not extensive). EDX analysis of the air side of the scale revealed only chromium (the presence of oxygen and/or nitrogen could not be detected); the Cr to Nb concentration ratio (Cr/Nb) was greater than 99. In contrast, for the Cr-6Nb specimens, layers similar in morphology and composition to those shown in Fig. 3 were limited to a fraction of the exposed surfaces. These layers corresponded to the upper gray scale observed visually (see Table 1). An example is shown on the left side of the micrograph in Fig. 4. The surface on the right side of the micrograph is an area where spallation occurred, and it contained substantially more Nb (Cr/Nb = 9.5). This was a general finding: the areas suffering oxide spallation had variable but significant niobium concentrations (up to Cr/Nb = 1), while the topmost layer always consisted solely of chromium and resembled the one shown in Fig. 4.

Fig. 1. Weight change versus exposure time for Cr -6 at. % Nb (6Nb) and -12 at. % Nb (12Nb) exposed in air at 950°C.

Table 1. Summary of visual observations of Cr-Nb specimens after isothermal exposure to air for 150 to 180 h.

Nb Conc. (at. %)	Exp. Temp. (°C)	% Area Showing Some Spallation	Appearance of Scale(s)
6	900	50	upper scale gray lower: brown
6	950	60	upper scale gray lower: blue/black/tan
12	900	<10	gray
12	950	<10	gray

Fig. 2. Weight change versus exposure time for Cr -6 at. % Nb (6Nb) and -12 at. % Nb (12Nb) exposed in air at 900°C.

Fig. 3. SEM of Cr - 12 at. % Nb exposed to air at 950°C for 168 h.

Fig. 4. SEM of Cr -6 at. % Nb exposed to air at 950°C for 164 h.

The SEM and EDX results indicate that more than one chemically distinct scale had formed on at least some of the alloys of this study. Optical examination of a polished cross section of Cr-12Nb oxidized at 900°C clearly showed the presence of a multilayer surface product (Fig. 5). Very little scale detachment was noted. The composite scale showed some porosity but no through cracking and was, in general, sound. The dark, thin, inner scale appeared to form preferentially on one phase of the alloy.

Discussion

Based on thermodynamic stability calculations,^{3,4} it is expected that multilayer scales of chromia overlying binary niobium oxides and, possibly, NbCrO_4 could exist on these alloys after exposure to air. As shown by the SEM results and the examination of the polished cross section, more than one product layer formed when the Cr-Nb alloys of this study were oxidized at 900 and 950°C. In addition, the EDX data suggest that the air-side layer was chromia since essentially only chromium cations were detected. Therefore, under the assumption that the observed layers are oxide products, the present scale data are consistent with thermodynamic predictions. (The formation of CrN cannot be definitely ruled out pending X-ray diffraction and oxidation experiments in pure oxygen.)

Fig. 5. Optical micrograph of polished cross section of Cr-12 at. % Nb exposed to air at 900°C for 168 h.

The thermogravimetric results in Figs. 1 and 2 clearly show that the overall weight gains in air are higher for the alloy with the lower niobium concentration. This is consistent with previous work (summarized in ref. 6), which showed that the ratio of oxidation rates of Cr-Nb to chromium decreased as the niobium concentration increased from 7 to 37 at. %. In addition, spallation was much more prevalent for the Cr-6Nb specimens (Table 1 and Figs. 3 and 4). Such a dependence of overall oxidation resistance on niobium concentration, and the capability to form multicomponent products, supports the supposition that a beneficial inner scale can be developed such that scaling is reduced and the adherence of the outer chromia-rich layer is improved. However, any explanation for improvement in oxidation resistance based on the possibility of an appropriate inner layer requires an understanding of the relatively complex microstructure of these alloys and how it changes with niobium content. As described by Takeyama and Liu,¹ the compositions of the two Cr-Nb alloys of this study place them in the hypoeutectic part of the Cr-Cr₂Nb two-phase

region, as shown by the microstructure of the 12Nb alloy (Fig. 5). The eutectic (17 at. % Nb) is composed of a Cr_2Nb matrix with a dispersion of the Cr-rich material, while the Cr-rich regions contain very fine Cr_2Nb precipitates.¹ Because the increase in niobium concentration from 6 to 12 at. % results in a higher volume fraction of the eutectic mixture, the poorer overall oxidation resistance of the 6Nb alloy appears to be related to the greater abundance of the Cr-rich phase. This suggests that the thin, dark product layer shown in the micrograph of Fig. 5, which forms preferentially over the Cr-rich regions, is less protective than the scale formed over the eutectic phase. Another, more protective, inner scale (not easily imaged in the optical microscope) may form over the eutectic mixture and lead to an improvement in oxidation resistance with increasing niobium concentration. More exhaustive analyses of scale products are required to make any definitive conclusions regarding the nature of the scales that are forming under the present conditions.

As shown in Figs. 1 and 2, several of the thermogravimetric curves showed definite stages of parabolic kinetics punctuated by abrupt increases in weight. This behavior was particularly apparent for the Cr-6Nb alloy oxidized at 900°C (Fig. 2). Such observations are normally indicative of scale cracking, which could expose more reactive underlying material, thus leading to the rapid kinetics associated with the initial stages of oxidation. Indeed, very similar weight change behavior has been reported for the oxidation of chromium.⁷ After a critical scale thickness is reached, cracking occurs to relieve accumulated stresses caused by the growth of the reaction product. The process can then start over again. At sufficiently high temperatures, the stresses may be relieved by plastic deformation rather than cracking, while at lower temperatures the onset of cracking can be delayed because of the longer time needed to reach the critical thickness.⁷ For isothermal scale cracking to occur, there normally must be growth of new oxide at a solid-solid interface.^{2,7}

By analysis of the weight changes between cracking events, parabolic rate constants at 900 and 950°C were determined from the thermogravimetric data (see Table 2). When necessary, several rate constants for one exposure were determined by fitting w^2 versus time curves to the intervals between apparent cracking events using linear regression analysis (see Eq. 2). In these cases, the rate constant varied randomly with total exposure time, and the values shown in Table 2 represent the average k_p . All the measured rate constants fall approximately in the center of the rather large range of k_p values (10^{-7} to 10^{-3} $\text{mg}^2/\text{cm}^4\text{s}$) reported for the oxidation of chromium at these temperatures.² The present alloys therefore

Table 2. Parabolic rate constants (k_p) for Cr-Nb specimens isothermally exposed to air for 150 to 180 h.

Nb Conc. (at. %)	Exp. Temp. (°C)	k_p ($\text{mg}^2/\text{cm}^4 \text{ s}$)
6	900	4×10^{-5}
6	950	4×10^{-5}
12	900	6×10^{-6}
12	950	2×10^{-5}

offer reasonable scaling resistance, problems with product cracking and spallation notwithstanding. However, as described above, such complications are also observed for chromium and, in many cases, can be avoided or overcome. Indeed, the similarity between the present results and some of the aspects of the growth, cracking, and spallation of scales on chromium supports the evidence that the oxidation resistance of these Cr-Nb alloys is strongly influenced by the volume fraction of the Cr-rich phase.

Although more detailed study is required, the present results do suggest several approaches to improved oxidation resistance of Cr-Cr₂Nb alloys. In particular, increasing the volume fraction of the eutectic phase at the expense of the Cr-rich region by using niobium concentrations of at least 12 at. % appears to reduce scaling and spallation. The use of purer starting materials may also reduce oxidation rates, as has been shown for chromium.⁸ Additionally, the chromium-like aspects of many of the present observations would suggest that some of the proven methods of improving scale adherence, such as microalloying and surface preparation,^{2,9} could be effective. Indeed, there are some initial indications that alloying can decrease spallation tendencies.¹⁰ It may also be possible to ameliorate scale cracking by alloying or restricting use of these materials to appropriate operating conditions (see above). If so, it may then be possible to maintain a sufficiently low oxygen partial pressure at the alloy-scale interface so that only protective NbO₂ or NbO, rather than Nb₂O₅, would form and remain stable.

Summary and Conclusions

The oxidation of Cr -6 and -12 at. % Nb alloys in air was studied at 900 and 950°C. Multilayer scales with outer chromium-rich layers were formed. 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. It was concluded that improvements to oxidation resistance could result from: (1) using a niobium concentration of at least 12 at. %, (2) exploiting proven methods for improving scale adherence on chromium and chromia-forming alloys, and (3) promoting the formation of a stable NbO₂ (or NbO) barrier layer.

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2.10 EVALUATION OF AUSTENITIC ALLOYS FOR ADVANCED STEAM CYCLES AND HOT-GAS CLEANUP SYSTEMS

R. W. Swindeman

INTRODUCTION

The fossil fuels power industry in the United States is experiencing a broad range of choices in meeting energy needs of the country. In the near term, life-extension with improved flexibility and reliability in existing plants is an issue of primary concern. In the longer range, improved efficiency will be needed, and this will come about by the development of advanced steam cycle and combined cycle power plants. The performance requirements for structural materials vary significantly from one application to the next, and the limiting performance criterion may be corrosion resistance, fabricability, or strength. Generally, the materials performance requirements become more demanding with increased service temperature, so efforts to evaluate materials may be separated on this basis.

Service to 600°C

Materials problems associated with the life-extension of existing pulverized coal power plants include erosion/corrosion of waterwall tubing, corrosion and stress-rupture of superheater tubing, fatigue and cracking in headers, stress-rupture and thermal stress-induced cracking of main steamline piping and reheat piping, similar and dissimilar metal weld failures, and cracking in turbine casings. The performance of new materials in some of these problem areas will provide guidance in the selection of materials for advanced steam cycles; hence, efforts are being made to collaborate with industry in evaluating life-extension.

For those plants that have failures in type 304 or 316 stainless steel piping, the use of the stronger type 316N stainless steel would permit thinner walls and reduce thermal stresses. In cooperation with South Carolina Electric and Gas Company and Toronado Energy Consultants, a piece of type 316N stainless steel main steamline piping was examined that had been in service at the A. M. Williams power plant for approximately 94,000 h at 540°C.¹ A field weld in the piping was included. Stress-rupture testing was undertaken to examine strength and ductility of base metal and weld metal. The rupture strength of the service-exposed type 316N stainless steel base metal was found to be 25% greater than type

316 stainless steel. Ductility of the service-exposed type 316N stainless steel was excellent. Values for elongation exceeded 20%, and the reduction of area values exceeded 30%.

Cracks were observed in the type 316 stainless steel welds, however, and these were thought to result from a combination of hot-cracks produced in the original field welds and lower creep strength in the filler metal. Additional work was performed at Oak Ridge National Laboratory (ORNL) to examine the use of controlled residual element (CRE) 16-8-2 stainless steel filler metal for joining the type 316N stainless steel piping.^{1,2} The CRE 16-8-2 stainless steel filler was found to be a good match for type 316N stainless steel. In Fig. 1, rupture data for the two materials are compared on the basis of the Larson-Miller parameter (LMP) for stress rupture.

Many of the advanced steam cycle plants are expected to have Gr-91 components. Superheater tubing, headers, and main steamline piping are potential applications for the steel. Gr-91 was originally developed for service about 540°C and is performing quite well at this temperature. For example, tubing placed in the superheater of the TVA Kingston Station was recently inspected after 8 years of service and showed no signs of degradation. Similar conclusions were reached after examination of tubing removed from the Tanners Creek Station. The use of Gr-91 in advanced steam cycle components operating at 600°C, however, requires more information about the long-time strength. Work has been undertaken at ORNL in cooperation with The Metals Properties Council to clarify the issue. Stress-rupture testing included heats of various tensile strengths, nitrogen levels, and product sizes. Tests were performed at higher temperatures and lower stresses. In Fig. 2, new data produced at ORNL are compared to the historical data on the basis of the log stress versus LMP for rupture life. Trends indicated that the allowable stresses currently in the American Society of Mechanical Engineers (ASME) Code Section II are representative of the alloy for temperatures to 600°C.

Service to 700°C

Advanced steam cycle plants will require superheater tubing to operate at temperatures approaching 700°C and at pressures in excess of 30 MPa. A high-temperature, ultrafine precipitate strengthened (HT-UPS) steel was examined for this application, and the evaluation has virtually been completed.³ One creep test remains in progress beyond 50,000 h at 700°C. Results indicated that the steel could meet the performance requirements if it were solution treated above 1175°C and subjected to at least 5% cold or warm work to

Fig. 1. Results of testing in support of life-extension of power plant: (a) comparison of the rupture strength of service-exposed 316N stainless steel with unexposed 316N and 316 stainless steels on the basis of the Larson-Miller parameter and (b) comparison of CRE 16-8-2 stainless steel replacement filler metal with unexposed 316N stainless steel.

promote the formation of fine MC precipitates. Cladding was required to protect against ash corrosion. With no Code status, it is unlikely that the HT-UPS steel will be used for pressure-bearing applications in the near future. However, industrial interest exists for its use in rocket components, sterling engines, and nuclear fuel cladding. These potential applications are being pursued.

Fig. 2. Results of tests on GR-91 steel to examine the strength at 600°C at 100,000h. New data confirm the trend observed when the Code allowable stresses were established.

A modified alloy 800 steel was evaluated as a potential material for the advanced steam cycle. This material contained the same MC-forming elements that contributed to the strength of the HT-UPS steel. The evaluation has been completed, and it was found that excellent strength could be developed by the thermal-mechanical processing scheme followed for the HT-UPS steel.⁴ With higher chromium and nickel, it was expected that the alloy would possess good steam and coal ash corrosion resistance. This proved to be the case, but the lack of Code status and the complicated chemistry and thermal-mechanical processing required for optimizing strength have worked against the commercialization of the alloy for general applications.

The weldability of both the HT-UPS steel and modified alloy 800 was of concern. Efforts were undertaken to select commercially available filler metals and to adjust the composition of the modified alloy 800 for better weldability. Both of these efforts met with some success. The CRE 16-8-2 stainless steel filler metal, mentioned earlier in connection

with its use for type 316N stainless steel, was found to be a good match for the HT-UPS steel. Sound welds were produced, and stress-rupture testing of welds has been extended to more than 20,000 h. For better corrosion resistance and strength, alloy 556 was also investigated. Stress-rupture data on weldments has been gathered to more than 10,000 h. In Fig. 3 the data base is summarized by the log stress versus LMP for rupture life.

Fig. 3. Results of stress-rupture testing of modified alloy 800 tubing. Data indicate excellent strength at low values of the Larson-Miller parameter, but there may be no advantage for the modified alloy at temperatures above 700°C.

Service Above 700°C

Components that may operate above 700°C include tubing for advanced steam topping cycles, tubing for heat recovery in fluidized bed combustion and gasifier combined cycles, and support plates and ducting in hot-gas cleanup vessels. Some components will be pressure bearing and will require Code-approved materials. Others that are structural will not require Code-approved materials, although these are often preferred. A variety of old and new alloys are being considered for use.

The possibility of extending the use temperature of the modified alloy 800 was considered. Testing of the alloys was extended to temperatures as high as 900°C, and the results are compared to the strength of alloy 800HT in Fig. 4. This is a plot of log stress versus the LMP for rupture life. It may be seen that at low values of the LMP the modified

alloy 800 has a significant strength advantage over alloy 800HT. This is attributed to the formation of a fine, stabilized MC-type precipitate in the modified alloy. At long times and high temperatures, however, the strength advantage may be lost. The arrows in Fig. 4 are located at the values of the LMP corresponding to 100,000 h at 760, 800, and 850°C. There are indications that the modified alloy may be comparable to alloy 800HT. One factor contributing to the degradation of the modified alloy 800 is a catastrophic oxidation phenomenon associated with the high molybdenum content. A revised composition with reduced molybdenum has been produced, and new testing at temperatures above 700°C will be undertaken.

Fig. 4. Results of stress-rupture testing of weldments in advanced austenitic alloys: (a) comparison of cross weldments in HT-UPS steel with the trend for type 316 stainless steel and (b) comparison of cross weldments in modified alloy 800 with the trend for 800HT base metal.

Under support from METC, two alloys were evaluated for tubesheets in hot-gas cleanup vessels for pressurized fluidized-bed combustion (PFBC) applications.^{5,6} These were alloys 333 and 556. Prediction of the performance of these alloys under highly cyclic service indicated that they would be marginal. One factor contributing to damage was the low yield strength of these materials at temperatures above 550°C. The possibility of using a nickel-aluminide was considered. Exploratory tensile, creep, and fatigue tests were performed on specimens from a casting of IC 396M. Data indicated that the aluminide had much greater yield strength and creep strength than conventional alloys, as shown in Fig. 5. The low-cycle fatigue life was less than that for alloys 333 and 556 at 871°C. An analysis of the performance of the aluminide in the tubesheet application will be undertaken after the completion of a few creep-fatigue damage interaction experiments.

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Fig. 5. Results of evaluations of cast nickel aluminide as a potential tubesheet material: (a) comparison of the temperature variation of the yield strength of IC 396M with the trend for alloys 556 and 333 and (b) comparison of the stress-rupture strengths on the basis of the Larson-Miller parameter.

Additional studies at temperatures in the range of 760 to 980°C have been undertaken to assist Code groups in developing criteria for setting allowable stresses for temperatures above 816°C. Experimentation involves low-stress creep tests to examine the shape of creep curves in the primary region and cyclic tests to examine cyclic softening and hardening. Initial studies involve alloy 800. Working with Westinghouse Electric Company and others, materials such as MA 263, modified alloy 800, modified 310 stainless steel, and newly developed nickel-chromium-iron alloys will be examined.

SUMMARY

1. Studies were completed of the potential of type 316N stainless steel for main steamline piping. Data for service-exposed base metal indicated good strength and ductility after many hours of service at 540°C. A CRE 16-8-2 stainless steel filler metal was found to be a good match for creep strength.
2. Stress-rupture testing of Gr-91 steel was undertaken to better define the strength of the steel at 600°C. It was found that the current stress allowables in the ASME Codes were representative of materials included in the original data base.
3. Research efforts were completed on austenitic alloys superheaters in an advanced steam cycle PC power plant. Testing of weldments was continued because of their general interest to industry. Both CRE 16-8-2 stainless steel and alloy 556 filler metals were tested to times exceeding 10,000 h.
4. Evaluation of modified alloy 800 was extended to temperatures above 700°C to support the need for materials in heat recovery and hot-gas cleanup systems that will experience service in the range of 760 to 925°C. A reduced molybdenum-containing modified alloy 800 was obtained for evaluation.
5. Efforts were begun to produce data needed to define acceptance criteria for new materials in pressure-bearing applications at temperatures above 816°C.

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2.11 COAL CONVERSION AND UTILIZATION PLANT SUPPORT SERVICES

J. R. Keiser

INTRODUCTION

During this period, support services were provided to two facilities. Assistance was provided to the staff of a coal gasification plant to help identify a means to eliminate corrosion in a distillation column. Corrosion samples provided by the Japanese were exposed in the two reactor vessels at the Wilsonville, Alabama, Coal Liquefaction Research and Development Facility. Because of the planned termination of operation of the Wilsonville facility, arrangements were made to retrieve all ORNL-supplied samples and to examine selected components.

DISCUSSION OF CURRENT ACTIVITIES

Coal Gasification

As described in the previous semiannual report, ORNL engineers twice visited the coal gasification plant near Beulah, North Dakota (formerly known as the Great Plains Coal Gasification Plant and now operated by the Dakota Gasification Company), to assist in the investigation of a serious corrosion problem in a phenol distillation tower. The phenol distillation tower is part of the phenol separation facility which was constructed to permit separation of phenol (hydroxybenzene) and cresylic acids (generally defined as a mixture of multiply substituted hydroxybenzenes so that the boiling point is in the range 220-250°C), both of which can be sold commercially. The phenol separation facility began operation in December, 1990, and operated for a total of about 130 days. The phenol distillation tower along with the other two towers in the facility are constructed of 304L stainless steel; nevertheless, considerable thinning of column trays was detected and operation was discontinued.

To assist in investigation of the corrosion problem, ORNL provided five racks of corrosion coupons which were exposed during a 24 day period in June and July when the phenol separation facility was operated. These racks of coupons were mounted on manway covers at five locations chosen to bracket the region where the most severe corrosion was

expected. The results indicated that the most severe corrosion occurred between trays 40 and 60 and probably reached about 0.76 mm/y (30 mil/y) on 304L stainless steel. Based on the coupon studies, Carpenter 20Cb3 and Incoloy 825 were identified as materials that were very resistant to corrosion in the phenol tower environment. The high molybdenum content austenitic stainless steels showed good corrosion resistance, and, quite surprisingly, carbon steel consistently corroded at a lower rate than the chromium-molybdenum steels.

Results of extensive studies conducted by personnel of the gasification plant provided guidance as to means to remove the corrodent from the process streams. The same corrosion coupons were exposed again to assess the effects of the efforts to remove the corrodent. The results which are shown in Tables 1-5 indicate the corrosion rates were significantly lower during the second exposure period. The extent of the corrosion rate reduction is shown graphically in Figures 1 and 2 where the corrosion rates for 5 Cr-1 Mo steel and 304L stainless steel for both exposure periods are shown. Although the corrodent removal process successfully reduced corrosion in the phenol tower, some evidence was reported that corrosion occurred in the vessels of the firm purchasing the phenol, so further studies are being conducted by the gasification plant staff.

Material	Corrosion Rate	
	mm/y	mil/y
2.25 Cr - 1 Mo	0.969	38.1
Carbon Steel	0.245	9.7
5 Cr - 1 Mo	0.081	3.2
Modified 9 Cr - 1 Mo	0.022	0.9
Type 410 Stainless Steel	0.013	0.5
7 Cr - 1 Mo	0.011	0.5
Type 317 Stainless Steel	<0.003	<0.1
Type 317LM Stainless Steel	<0.003	<0.1
Ferralium	<0.003	<0.1
Type 310 Stainless Steel	<0.003	<0.1
Incoloy 825	<0.003	<0.1
Type 316L Stainless Steel	<0.003	<0.1
Carpenter 20Cb3	<0.003	<0.1
Type 304L Stainless Steel	<0.003	<0.1
Type 321 Stainless Steel	<0.003	<0.1

Table 1. Calculated corrosion rates for coupons exposed 744 hours at the manway below tray 1 in the phenol distillation tower of the Dakota Gasification Company's Beulah, North Dakota plant.

Material	Corrosion Rate	
	mm/y	mil/y
Carbon Steel	0.043	1.7
Type 304L Stainless Steel	0.026	1.0
Type 321 Stainless Steel	0.020	0.8
2.25 Cr - 1 Mo	0.019	0.7
5 Cr - 1 Mo	0.003	0.1
Ferralium	0.003	0.1
Type 410 Stainless Steel	0.003	0.1
7 Cr - 1 Mo	<0.003	<0.1
Modified 9 Cr - 1 Mo	<0.003	<0.1
Type 317 Stainless Steel	<0.003	<0.1
Incoloy 825	<0.003	<0.1
Type 317LM Stainless Steel	<0.003	<0.1
Carpenter 20Cb3	<0.003	<0.1
Type 310 Stainless Steel	<0.003	<0.1
Type 316L Stainless Steel	<0.003	<0.1

Table 2. Calculated corrosion rates for coupons exposed 744 hours at the manway located at tray 20 in the phenol distillation tower of the Dakota Gasification Company's Beulah, North Dakota plant.

Material	Corrosion Rate	
	mm/y	mil/y
Ferralium	0.021	0.8
Type 310 Stainless Steel	0.018	0.7
Type 304L Stainless Steel	0.011	0.4
Type 317 Stainless Steel	0.006	0.2
Type 316L Stainless Steel	0.005	0.2
Type 321 Stainless Steel	0.004	0.2
Type 317LM Stainless Steel	<0.003	<0.1
Incoloy 825	<0.003	<0.1
Carpenter 20Cb3	<0.003	<0.1
Type 410 Stainless Steel	<0.003	<0.1
Modified 9 Cr - 1 Mo	<0.003	<0.1
7 Cr - 1 Mo	<0.003	<0.1
5 Cr - 1 Mo	<0.003	<0.1
2.25 Cr - 1 Mo	<0.003	<0.1
Carbon Steel	<0.003	<0.1

Table 3. Calculated corrosion rates for coupons exposed 744 hours at the manway located at tray 40 in the phenol distillation tower of the Dakota Gasification Company's Beulah, North Dakota plant.

Material	Corrosion Rate	
	mm/y	mil/y
Carbon Steel	0.078	3.1
Type 321 Stainless Steel	0.037	1.4
Type 304L Stainless Steel	0.032	1.2
Ferrallium	0.017	0.7
Type 310 Stainless Steel	0.013	0.5
Type 316L Stainless Steel	0.011	0.4
Modified 9 Cr - 1 Mo	0.010	0.4
2.25 Cr - 1 Mo	0.008	0.3
5 Cr - 1 Mo	0.007	0.3
7 Cr - 1 Mo	0.005	0.2
Type 410 Stainless Steel	0.004	0.2
Type 317 Stainless Steel	<0.003	<0.1
Carpenter 20Cb3	<0.003	<0.1
Incoloy 825	<0.003	<0.1
Type 317LM Stainless Steel	<0.003	<0.1

Table 4. Calculated corrosion rates for coupons exposed 744 hours at the manway located at tray 60 in the phenol distillation tower of the Dakota Gasification Company's Beulah, North Dakota plant.

Material	Corrosion Rate	
	mm/y	mil/y
Carbon Steel	0.013	0.5
Type 304L Stainless Steel	0.011	0.5
Type 321 Stainless Steel	0.010	0.4
Modified 9 Cr - 1 Mo	0.007	0.3
Type 410 Stainless Steel	0.007	0.3
5 Cr - 1 Mo	0.005	0.2
7 Cr - 1 Mo	0.004	0.2
Type 310 Stainless Steel	0.003	0.1
Type 316L Stainless Steel	<0.003	<0.1
Ferrallium	<0.003	<0.1
Type 317 Stainless Steel	<0.003	<0.1
Carpenter 20Cb3	<0.003	<0.1
Type 317LM Stainless Steel	<0.003	<0.1

Table 5. Calculated corrosion rates for coupons exposed 744 hours at the manway located at tray 80 in the phenol distillation tower of the Dakota Gasification Company's Beulah, North Dakota plant.

Fig. 1. Calculated Corrosion Rates for 5 Cr-1 Mo Steel

Fig. 2. Calculated Corrosion Rates for 304L Stainless Steel

Coal Liquefaction

An agreement between the U.S. Department of Energy (DOE) and the Japanese Agency for Industrial Science and Technology (AIST) calls for each country to provide corrosion samples for exposure in coal liquefaction plants operated by the other country. On behalf of AIST, two sets of samples were sent to ORNL where they were measured, weighed, and mounted on racks suitable for the two reactor vessels in the Wilsonville facility. These sample racks were taken to Wilsonville where they were exposed in the reactors for several months. The samples were removed from the reactors during March and returned to ORNL for examination. Fig. 3 shows the samples following exposure. Characterization of the samples is underway, and the results will be given in the next semiannual report.

Fig. 3 Samples Following Exposure

A set of samples prepared by ORNL personnel for exposure in the Japanese coal liquefaction reactor were shipped to Japan in early September and were exposed for 50-100 days during the fall. These samples are currently being examined by the Japanese.

Because operation of the Wilsonville coal liquefaction is being terminated, plans are being made for ORNL personnel to travel to Wilsonville to inspect selected vessels, collect all ORNL-supplied samples, and select components for further examination. This trip is expected to be made in April or May.

2.12 CLEAN COAL PROGRAM MATERIALS SUPPORT

J. R. Keiser

INTRODUCTION

This project is intended to provide materials support to Clean Coal Technology Program contractors. This support can be provided in several forms; recommendation of materials or evaluation of material selections, supply of samples for corrosion/erosion monitoring, and analysis of components after exposure to assess the extent of interaction with the environment and, when appropriate, the cause for failure.

DISCUSSION OF CURRENT ACTIVITIES

A review was conducted of the materials selected for the fans and heat exchangers of the Selective Catalytic Reduction (SCR) project to be located at Gulf Power Company's Plant Crist Unit 5 near Pensacola, Florida. This prototype SCR plant will be equipped with three large (5000 scfm baseline flow) parallel SCR reactor trains and six small (400 scfm baseline flow) parallel trains. For the large trains, three large exhaust gas fans will be required; one for each train. Two of the large reactors will be equipped with Ljungstrom type air heaters down stream of the reactor vessels, while the third large reactor will have a heat pipe heat exchanger. The gas stream from each air heater will pass through a cyclone dust collector before entering each fan. The flue gas that will be processed in the SCR facility will be drawn from the main unit gas stream upstream of the main unit hot side precipitator. Thus, the hot flue gas entering the exchangers will contain particulate matter and potentially corrosive components such as SO_2 , SO_3 , HCl , and NH_3 .

In addition to the three large fans, two fans will be required for the six small reactors; one fan for each three reactors. The flue gas supply for one of these small reactors will come from downstream of the main unit hot side precipitator, while the remaining five reactors will use the same supply source as the large reactors; upstream of the precipitator.

A single hot air fan will be used to pull ambient air through the two Ljungstrom air heaters and also the single heat pipe air heater. Another fan will be needed to supply ambient air through a manifold to the ammonia injection system for each of the nine reactor streams.

The operating conditions for each component were reviewed, and the potential for corrosion and/or erosion-corrosion was assessed. Based on this assessment, recommendations were made on the siting of samples and the selection of materials for the samples.

3. ENVIRONMENTAL ANALYSIS SUPPORT

C. R. Boston

INTRODUCTION

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 Program. A key activity was the preparation for PETC of a preliminary 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 Program. Assistance also was provided to the DOE Office of Fossil Energy in evaluating the environmental aspects of projects proposed for cost-shared funding under the fourth round of the Clean Coal Program.

3.1 ENVIRONMENTAL SUPPORT TO THE CLEAN COAL PROGRAM

R. L. Miller

Work during this six-month period again focused on assisting DCE's Pittsburgh Energy Technology Center (PETC) in the preparation 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 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 EIS is notable because it is the first site-specific EIS prepared for the Clean Coal Program. The draft EIS is undergoing final revisions prior to issuance by DOE for public comment.

3.2 ENVIRONMENTAL SUPPORT TO METC R&D PROJECTS

R. L. MILLER

ORNL is assisting METC in the preparation of an Environmental Assessment for the proposed Gasification Product Improvement Facility (GPIF) near Morgantown, West Virginia. The near-term GPIF goal is to develop an air-blown, fixed-bed gasification system capable of processing high-swelling coals and reducing dependence on add-on subsystems. Longer-term goals include the development of an advanced metal oxide hot gas cleanup system and verification of the integrated operation of the improved gasifier, the advanced cleanup process, the low-BTU combustion gas turbine, and the advanced gasification concepts. The proposed facility would be part of METC's R&D program. The EA is about 25% complete, but is currently on hold awaiting information from the sponsor.

Work was initiated on an Environmental Impact Statement for the proposed Pressurized Circulating Fluidized Bed (PCFB) Repowering Project as part of the Des Moines Energy Center located in Pleasant Hill, Iowa. This project is one of those selected in the Third Round of proposal solicitations for the Clean Coal Technology Program. Of the many active CCTP projects, only two have required EISs. The others have required only EAs. ORNL is assisting DOE on both EISs, the other being the Healy, Alaska project discussed in Section 3.1. The 70-MWe coal-fired generation facility would demonstrate a PCFB combustor by repowering an existing steam turbine with a single PCFB module operated in a combined-cycle mode. The total cost of the proposed project is estimated at \$203 million with DOE's share being about \$93.2 million.

3.3 OIL RESEARCH PROGRAM ENVIRONMENTAL SUPPORT

R. L. MILLER

ORNL is assisting DOE/Fossil Energy (FE) in the preparation of a Programmatic Environmental Assessment (PEA) for FE's proposed Oil Research Program. The United States has produced more oil than any other nation in history, but twice as much oil as has been produced still remains unrecovered in known reservoirs (340 billion barrels). While U.S. proven reserves and production have declined since 1970, imports have risen dramatically because of the lack of commercially-proven, cost-effective technologies to harvest the remaining, known oil under present economic conditions. DOE's proposed Oil Research Program, based on current policies and recent assessments of the oil industry and national research needs, would build upon earlier programs, but would entail a more comprehensive and timely approach. The Program would implement a research, development, and demonstration plan in collaboration with the states, industry, and the academic community, focusing on reducing the technical and economic constraints on producibility to tap into the huge resource remaining in known reservoirs. Research would address the near-term (within 5 years) and mid-term (within 10 years) needs of the oil industry, complementing the historical emphasis on long-term research and development. The results of the Program's activities would be disseminated to the states and industry. An important aspect of the PEA would be to assess the environmental impact of advanced recovery techniques and develop mitigation techniques if found to be necessary. Work on the PEA was initiated in this reporting period and is now well underway with completion expected in the fall of 1992.

3.4 ENVIRONMENTAL SUPPORT TO DOE/FOSSIL ENERGY

C. R. BOSTON

ORNL is assisting DOE/Fossil Energy in preparing a programmatic Action Description Memorandum (ADM) for Morgantown Energy Technology Center's (METC's) Research and Development (R&D) projects. The ADM must consider potential environmental impacts, including cumulative impacts, of continuing METC's R&D program which consists of over 300 individual contracts with a wide variety of organization spread over the United States. The ADM could lead to a decision by DOE to prepared a formal National Environmental Policy Act (NEPA) document (e.g. a programmatic Environmental Assessment) or that the program qualifies for a Categorical Exclusion and no futher NEPA reviews are required.

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. Activities are also continuing on the study of mild gasification of coal.

4.1 BIOLOGICAL CATALYSTS IN ORGANIC MEDIA

C. D. Scott

INTRODUCTION

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. This approach was shown to permit the shifting of chemical equilibria and to facilitate unusual reactions not commonly observed in aqueous medium. In addition, catalysis in organic solvents allows the interaction of the biological catalysts with substrates that are not normally water-soluble. Demonstration of catalysis in nonaqueous media are consistent with the retrospective realization that many biological reactions take place in nature within hydrophobic environments, i.e., lipid-based cell membranes, or on hydrophobic surfaces such as leaves.

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 immobilize microorganisms into a controlled microenvironment 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

It has previously been shown that enzymes or other proteins can be modified by attaching a chemical moiety to reactive groups on the protein molecule such as the "free amino" groups. When the chemical additions are hydrophobic in nature, the resulting modified enzyme will also be more hydrophobic and probably more soluble in less polar organic solvents. It is very important to carry out such modifications without adversely affecting the activity of the biocatalyst which may also be associated with some of the protein active sites, so the chemical reactions must be selective. This is the rationale for continuing research on the modification of enzymes to enhance solubilization in organic media.

As previously shown, 2,4 dinitrofluorobenzene (DNFB) can be used as a reagent to add dinitrophenyl (DNP) groups to enzymes, and, thus, make them more hydrophobic and more soluble in nonpolar organic solvents. The chemistry of this addition appears to be interaction with free amine groups on the enzyme. Work is continuing on optimizing this chemical conversion to enhance solvent solubility while maintaining enzymatic activity. The two model enzymes are hydrogenase isolated from *Proteus vulgaris* with techniques previously described and bovine cytochrome c obtained from Sigma Chemical Co. In order to protect enzymatic activity, two approaches are being studied: (1) use relatively mild reaction conditions in which there is incomplete interaction with all of the active sites; and (2) protecting the active sites by prior adsorption of an appropriate substrate.

The range of experimental conditions being studied include a mixture of water and ethyl alcohol with the ethanol fraction varying from 28 to 65% that contained 0.1 to 3 vol% DNFB buffered to a pH of approximately 8.5 with a 7 mM phosphate buffer and/or NaHCO_3 . The reaction was carried out in shake flasks at ambient temperature ($25 \pm 1^\circ\text{C}$) in the presence of air for reaction times of 0.5 to 2 h. After the primary reaction, the pH was reduced to 7 by the addition of HCl and the reaction mixture was dialyzed overnight against 50 times the volume of the same ethanol-water-buffer mixture at a pH of 7 but without DNFB using a cellulose membrane with a molecular weight cut-off of 12-14,000 Daltons (Spectra/Por dialysis membrane from Spectrum Medical Industries, Inc.). After dialysis, the modified enzymes were converted to the reduced state by the addition of 5 mg/mL sodium dithionite and then lyophilized and stored under N_2 until used.

At the most severe conditions of reaction (3 vol% DNFB and 2h of contact time), a portion of the modified enzyme actually precipitated and was recovered as a yellow solid that had very low water solubility. At milder conditions (0.1 vol% DNFB and 0.5 h of contact time), the modified enzyme was still soluble in the alcohol-water solution but even after dialysis the solution had a yellow color indicative of DNP addition.

As previously shown, modification of enzymes with DNFB resulted in higher solubilization in organic solvents which increased as the hydrophobicity of the solvent decreased. The solubility of the unmodified enzyme also increased as the hydrophobicity of the solvent decreases, but it varied from undetectable in benzene and toluene to barely detectable in pyridine and dioxane. Unfortunately, there was appreciable enzyme deactivation in the solvent of lowest hydrophobicity.

It has now been shown that the degree of dinitrophenylation affects the solubilization of the modified enzyme in organic solvents. For example, with a 0.5 h reaction time, as the concentration of DNFB in the reaction solution was increased from 0 to 0.67 vol %, there was a corresponding increase in the DNP content and solubilization in benzene reaching a maximum value of 9.2 mg/mL (Fig. 4.1). However, there was also a corresponding decrease in the enzyme activity presumably due to the addition of DNP in the region of the active sites. At the higher DNFB concentration, the activity was only 40% of the original value. This could be partially alleviated by the adsorption of an appropriate substrate such as benzyl viologen to the enzyme mixture prior to the addition of the DNFB. For example, when 0.17% DNFB was used to react with hydrogenase for 30 min, the biocatalytic activity was only 86.5% of the starting material. But, when 20 mM benzyl viologen was added to the reaction mixture, the resulting activity of the modified hydrogenase was increased to the original value. The preadsorption of the substrate apparently partially protected the active site from interaction with the phenylizing reagent. Results at other concentrations have been somewhat variable, so additional research will be required to fully understand and use this technique.

ORNL Research on Microbial Biotransformations in Organic Media

Enzymatic catalysis within organic media is a well-known phenomenon. These catalytic events are typically single-step reactions mediated by isolated enzymes. Stabilization of the enzymes within nonaqueous milieu can be a problem. In nature, many intracellular enzymes are stabilized by localization within or adjacent to the membranes of living organisms. Intact

Fig. 4.1. The effect of DNFB concentration on enzyme solubility in benzene and enzyme activity when reacted with hydrogenase for 0.5 h in a water-ethanol mixture at a pH of 8.5 and a temperature of 25°C.

microorganisms may thus be viewed as multifunctional catalytic units. Microorganisms are always found in nature within aqueous milieu, either in a bulk aqueous phase or at the interface between an aqueous and a nonaqueous phase. Microbial activity within wholly nonaqueous phases has not been demonstrated. However, microbial attack on petroleum and other nonpolar materials is well known. These reactions occur at the oil-water interface. Reactions of this type, i.e. those carried out in biphasic systems, may be equally relevant to the processing of coal or coal-derived materials. These reactions may be particularly important in the beneficiation and/or detoxification of coal tars.

The current work is designed to test the feasibility of microbial processing of coal-derived liquids within biphasic systems, with emphasis on the transformation of polyaromatic compounds. Sulfur removal from dibenzothiophene (DBT), a heterocyclic coal model compound, is being used as a model system in this effort. *Paecilomyces* sp. TLi, a fungus isolated from coal and previously shown to modify DBT, is the focus of this work. This organism catalyzes a sulfur-specific attack on DBT, with formation of a dihydroxybiphenyl. A minor side reaction has also been detected that leads to unknown products, possibly including some formed by ring cleavage. The goal of this work is to demonstrate activity against DBT in the presence of organic media and to assess the specificity of the reaction under these conditions.

Preliminary effort has focused on the development of biphasic systems for use in subsequent tests. Benzene was chosen for use in this work due to DBT's enhanced solubility in this solvent. The aqueous phase consisted of culture medium typically used to grow the organism. DBT transformation had previously been demonstrated in this medium.

Current work has focused on addressing the several technical challenges associated with the proposed test system. In prior tests, DBT, which is insoluble with water, had been introduced into cultures as a solution in dimethylformamide (DMF). The resultant dispersion was stabilized with Tween 80, a surfactant. Control experiments, designed to determine the effect of benzene on the standard assay system, were confounded by the failure to achieve phase separation. This failure was presumably due to the presence of Tween 80. Removal of the Tween 80 resulted in changes in the organism's macroscopic appearance. Morphological changes in fungi generally reflect changes in enzyme complement as well. Finally, in the presence or absence of Tween 80, the organism failed to remain at the benzene:water interface. This behavior suggests that catalysis, if any, would occur strictly within the aqueous layer. No DBT transformation products were detected in any of the cultures tested. The various problems noted above make it difficult to interpret these experimental results. Efforts to resolve these technical problems are ongoing. It is possible that the desired reactions were only partially inhibited under the test conditions. However, the thin-layer chromatographic assay routinely used in this work may not be sufficiently sensitive to detect products formed. Gas chromatography was previously shown to be inappropriate for use in the analysis of DBT metabolites due to their thermal lability. A new, liquid chromatographic assay is therefore under development.

MIT Research on Oxidoreductive Processes Relevant to the Conversion of Coal Catalyzed by Enzymes in Organic Solvents

It has been discovered that not only horseradish peroxidase but different non-enzymic hemoproteins, including (the waste protein) bovine blood hemoglobin, readily oxidize dibenzothiophene (DBT, an accepted model of organic sulfur in coal) with hydrogen peroxide. Specifically, we showed that the oxidation of DBT to its 5-oxide (DBTO) and/or sulfone (DBTS), catalyzed by hemoglobin, occurred in an aqueous buffer containing 25% (v/v) of a water-miscible organic solvent (n-propanol, acetonitrile, or ethanol). Surprisingly, the degree of DBT's final conversion depended on the hemoglobin concentration, being 5, 56, and 99% at 0.25, 2.5, and 25 μ M protein, respectively. In other words, the reaction stopped prior to full depletion of DBT, suggesting protein inactivation during the reaction.

We decided to test whether the stability of hemoglobin might be greater at high concentrations of an organic solvent. Also, the solubility of DBT should increase in such a system. Therefore, during this reporting period, research has been conducted on the ability of hemoglobin to catalyze the oxidation of DBT by hydrogen peroxide in predominantly organic media. We found that this oxidation occurred even in neat organic solvents. (No appreciable DBT transformation was detected without protein or hydrogen peroxide.) Unfortunately, in such media the reaction also stopped before the depletion of DBT; in fact, the maximal degree of conversion in them was less than in water. As an illustration, the time course of the oxidation of DBT to DBTO in neat ethanol (in the presence of 0.14% of water brought in with hydrogen peroxide) is shown in Fig. 4.2. As one can see, the maximal conversion of DBT is 30%, i.e., 2.5 times lower than in aqueous solution at the same concentration of hemoglobin.

Substrates often protect enzymes from inactivation. Therefore, we examined the hemoglobin-catalyzed oxidation of DBT to DBTO in ethanol at higher concentrations of the substrate (readily soluble in this solvent but not in water). As one can see in Fig. 4.3, the higher the concentration of DBT, the more DBTO is formed. The turnover number ($[\text{DBTO}]/[\text{Hb}]$) of the reaction also increases, which means that the reaction accelerates and/or protein stabilization occurs. It is seen in Fig. 4.3, however, that an increase in the DBT concentration exceeds that for DBTO, and, consequently, the maximal degree of conversion for the oxidation reaction. These data point to no stabilization of hemoglobin by the substrate in the system described.

We also tested the possibility that the observed inactivation of hemoglobin in the course of oxidation of DBT involves molecular oxygen. To this end, in a separate experiment O_2 was excluded from the system. It was found that there was no significant difference either in kinetics or in the maximal level of substrate transformation when the oxidation of DBT by hydrogen peroxide, catalyzed by hemoglobin, was carried out under anaerobic instead of aerobic (under argon instead of air) conditions. Thus, molecular oxygen does not play a role in hemoglobin inactivation during the reaction.

Mechanism of the discovered oxidation of DBT by hydrogen peroxide catalyzed by hemoglobin is unclear. In fact, only few examples of S-oxygenations catalyzed by hemoproteins have been reported. These include thioanisole and thiobenzamide oxidation catalyzed by horseradish, lacto-, and chloro-peroxidases. Although the mechanism of the enzymatic oxygen incorporation into such sulfur-containing compounds is still obscure, it is thought to occur via a free-radical pathway involving a hydrogen transfer. Thus, solvent molecules could participate in

Fig. 4.2. DBT (●) oxidation to DBTO (O) by hydrogen peroxide catalyzed by hemoglobin in ethanol containing 0.13% water). Hemoglobin was lyophilized from aqueous solution of pH 4.1. Other conditions: $[H_2O_2] = 10\text{mM}$, $[Hb] = 25\mu\text{M}$, 30°C .

Fig. 4.3. DBTO concentration (●), degree of conversion (▽), and turnover number ($[DBTO]/[Hb]$) (O) in the oxidation of DBT by hydrogen peroxide catalyzed by hemoglobin in ethanol (containing 0.13% of water) as a function of the DBT concentration. Hemoglobin was lyophilized from aqueous solution of pH 4.1. Other conditions: $[H_2O_2] = 10\text{mM}$, $[Hb] = 25\mu\text{M}$, 30°C .

this reaction by means of hydrogen bonding, and hence polarity and "acidity" of the reaction medium may be important. Consequently, the oxidation of DBT by hydrogen peroxide, catalyzed by hemoglobin, was studied in neat organic solvent of different classes (e.g., primary, secondary, and tertiary alcohols, as well as diols, amides, ethers, and esters) containing 0.13, 1, or 5% (v/v) of aqueous buffer. The dependence of the concentration of DBTO formed on the E_T^N parameter reflecting solvent polarity is shown in Fig. 4.4. For the water contents of 0.13 and 1%, there is no detectable oxidation of DBT in solvents with E_T^N below 0.4. Above this E_T^N value, a correlation exists between the concentration of DBTO and solvent polarity: the higher the solvent polarity, the more product is formed. Basically, the DBT oxidation occurs only in protic solvents, which is consistent with the aforementioned involvement of solvent's protons in this reaction. From the observed difference (Fig. 4.4) between the solvents with 1 and 5% of water, it follows that the greater the water content of the system, the wider the range of solvents which could be used to carry out this reaction.

As mentioned above, solvent acidity could play a role in the oxidation of DBT. For example, alcohols have an acidic nature although weaker than that of water. The following order of acidity holds: water > primary alcohols > *sec*-alcohols >> *tert*-alcohols. We found that the degree of the substrate transformation for the series of isomeric butanols (primary, secondary, and tertiary) (points 13, 17, and 20 in Fig. 4.4), as well as for *n*- and *iso*-propanols (points 12, and 16 in Fig. 4.4), changed in the same order. Moreover, for the series of homologous primary alcohols, the degree of DBT transformation correlates with their pK_a values, namely, the greater the solvent acidity, the higher the degree of DBT conversion. Among all the solvents used, water possesses the highest polarity and the strongest acidic nature. Hence, one can expect an increased level of the substrate transformation when the water content in the mixture is increased, which is indeed what was observed (Fig. 4.5). Furthermore, it is seen in Fig. 4.5 that the dependence of the degree of conversion of DBT on the water content is quite distinct for various solvents, although the overall trend for all of them is that the higher the water content, the greater the transformation of DBT.

We conclude that the optimal reaction medium for the oxidation of DBT is water. In the later, however, poor solubility of the substrate may present a problem. We attempted to address it using two-phase systems of water/water-immiscible organic solvents. Water content was 10, 50, and 75% (v/v) in *tert*-butyl methyl ether, toluene, or ethyl acetate. In all cases, DBT partitioned into the organic phase, and no appreciable transformation of the substrate ensued. When we used

Fig. 4.4. Product formation ($[\text{DBTO}] / [\text{DBT}]_0$) in the reaction of oxidation of DBT by hydrogen catalyzed by hemoglobin as a function of the E_T^N polarity parameter of organic solvents containing 0.13 (∇), 1 ($\bullet$), and 5 (O) % (v/v) of water. Other conditions: $[\text{H}_2\text{O}_2] = 10\text{mM}$, $[\text{Hb}] = 25\mu\text{M}$, 30°C .

a biphasic system containing only 25% (v/v) of n-butanol, the oxidation of DBT stopped at 5% of conversion. In the monophasic system consisting of n-butanol with 5% (v/v) of water, we obtained 14% of DBTO (Fig. 4.4). Thus, the separation of the substrate from protein does not lead to a greater degree of DBT transformation.

Fig. 4.5. Oxidation of DBT by hydrogen peroxide catalyzed by hemoglobin in different organic solvents as a function of water content: a - ethylene glycol, b - ethanol, c - propanol, d - acetonitrile. Experimental conditions: $[Hb] = 25\mu M$, $[H_2O_2] = 10mM$, $[DBT] = 0.23mM$, 20mM acetate-phosphate buffer, pH 4.1, 30°C.

In order to shed light on the mechanism of hemoglobin inactivation during its reaction with DBT and hydrogen peroxide, we examined the visible spectrum of the protein in ethanol. The absorbance at the Soret band decreased approximately 10 times in the first 15 min of the reaction in ethanol; in particular, the wavelength of the maximal absorbance shifted toward the UV region. These data suggest that the heme becomes more exposed to the solvent, and that chemical modification of the heme may have occurred. In recent publications, suicide inactivation of hemoproteins by some reactants has been described. One of the likely reasons for this inactivation is an attack of the porphyrin ring by a reaction intermediate leading to a chemical conjugate. Another possibility is the oxidation of methylene bridges of the heme by hydrogen peroxide. Specific binding of solvent molecules acting as ligands of Fe^{3+} of the heme also cannot be excluded. In our future work, we will investigate the exact mechanism of the hemoglobin inactivation observed and use it to develop a rational stabilization strategy.

4.2 ADVANCED BIOREACTOR SYSTEMS

T. C. Scott

INTRODUCTION

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 gaseous-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 first three of these four items.

Axial pressure drop data have been obtained for fluidized-beds which are a combination of two of the four coal fractions described in earlier reports. Figure 4.6 shows a plot of such data for a bed which consists of a mixture of 50 micron- and 70 micron- diameter coal particles. Included are pressure data from six different liquid flow rates. It is interesting to note that each of the pressure profiles shows a distinct curvature which is characteristic of polydisperse systems which are undergoing some degree of particle segregation in the bed. Monodisperse systems show no such curvature as the particles are evenly distributed along the axis of the column. It

is of particular interest to note the apparent break in the curve at the highest liquid velocity (0.0156 cm/s). Without corresponding particle distribution data, it is not possible at this time to tell if this represents true segregation behavior or is simply an erroneous measurement.

Several methods have been investigated for determination of the particle distribution along the bed. Candidate methods which were considered are: acoustics, ultrasonics, and laser light scattering. Each of these approaches has serious drawbacks for the coal-particle suspensions. Generally, these will not work because the suspension is too dense or too polydisperse to get a clear discernable signal. A different approach involves chemically binding a fluorescent dye to one of the particle sizes and taking a video image of a portion of the bed. Suitable filters can be used on the camera so that only the fluorescent particles will show-up. This image can then be digitized and scanned to determine the fraction of the two particle sizes at a given point in the bed. Preliminary attempts at this technique have not been very successful. Either the dye does not bind to the coal, does bind but loses the capability to fluoresce, or leaches off the coal when in prolonged contact with water.

Fig. 4.6. Pressure drop as a function of vertical position in a liquid-fluidized bed of coal. Bed consists of 50 micron- and 70 micron-diameter coal particles.

Impulse changes in the electrical conductivity of the liquid phase will be used to determine liquid-phase dispersion characteristics. Conductivity probes have been machined into the wall of special column inserts to allow measurement of the transient signal. The electrical contacts are flush with the wall of the column so as to minimize effects on flow in the system. The signals from these probes will be recorded on the computer data acquisition system along with the pressure drop-data to help more clearly determine behavior of the bed. The standard approach of the method of moments will be used to determine the effective liquid-phase diffusivity from the transient conductivity plots.

WSU Modeling Research

The mathematical modeling of the hydrodynamics of the liquid fluidized bed containing coal particles of two different sizes continue to be the goal of the ongoing research efforts at WSU. In addition, we have taken advantage of some of our specialized equipment to obtain the particle size distribution of various size fractions of coal particles being used in the experimental program at ORNL. The important aspect of modeling studies will be discussed first and the model predictions will be compared with experimental data available from ORNL. The particle size distribution analysis of representative fractions of coal particles will be discussed later.

Mathematical Modeling

Unlike the fluidization of the mono-sized particles, binary-solid fluidization shows a tendency towards segregation. This behavior is marked by larger coal particles predominantly occupying the lower region of the bed while the smaller coal particles are present in the upper region of the bed in greater concentrations. Between these two regions of relatively pure components, the concentration of the individual particle species gradually changes. Such a behavior is attributed to two counteracting mass-transport mechanisms of dispersion and convection. The diffusion or more precisely the dispersion of particles tends to eliminate the presence of concentration gradient of the individual coal particle species. The convection, on the other hand, tends to cause segregation of different-sized coal particles in the fluidized bed. It is important to note here that the effective convective flux under discussion here is not caused by the motion of the fluidizing medium in the present case of semi-batch fluidization. Rather it is

the force balance considerations which impart motion to a particle when it is not present in the neighborhood of like particles. What this implies is that a large coal particle, for example, when present in the bottom of the bed in the vicinity of other large particles at a particular value of voidage will possess zero effective velocity. On the other hand, the same large particle when present in the neighborhood of small coal particles will have an effective velocity, henceforth referred to as the segregation velocity, that will tend to bring it to the lower region of the bed mainly consisting of large particles.

The modeling of the aforementioned phenomena has generated significant interest in the literature. A brief review of important studies in this area was given in the last report and a model was proposed based on the existing literature information. During the current reporting period, the work continued on developing better models for mixing and segregation characteristics of the coal particles of different sizes in the liquid fluidized bed. The emphasis was to correctly apply the basic mass balance approach to derive the model equations. The present model accounts for the segregation flux of particles as being the contribution of both the large as well as small coal particles while no such contribution is made by the upward flowing fluidizing medium.

Model Development

In this section, the steps involved in the derivation of the final modeling equation will be briefly outlined. The total mass flux, N_i , of particle species 'i' as a result of dispersion and convection mass transport mechanisms is given by

$$N_i = -\rho D_i \left(\frac{d\omega_i}{dz} \right) + \rho U_s \omega_i \quad (1)$$

where, ρ is the bulk density, ω_i is the mass fraction of species i, D_i is the dispersion coefficient of 'i' and U_s is the over-all mass velocity given by

$$U_s = \omega_a U_{sa} + \omega_b U_{sb} \quad (2)$$

Here, subscripts 'a' and 'b' stand for the two particle species present in the bed and U_{sa} and U_{sb} are the segregation velocities of particle species 'a' and 'b', respectively. In order to calculate the value of the individual segregation velocities, one of the available relative velocity correlations could be employed. In terms of Richardson and Zaki correlation, we can write

$$U_{ri} = U_f - U_{ti} = U_{ti} \epsilon^{n_i-1} \quad (3)$$

where, U_{ri} is the particle relative velocity, U_{ti} is the particle terminal velocity, U_f is the fluid velocity and ϵ is the bed voidage fraction and n_i is the Richardson-Zaki index. The fluid velocity can be evaluated from the mass balance considerations. The value of individual segregation velocities from eqn (3) can then be used to evaluate over-all segregation velocity in eqn (2). At steady-state,

$$\frac{dN_i}{dz} = 0 \quad (4)$$

Substituting the expression for N_i from eqn (1) in the above equation and using the continuity requirement finally gives,

$$\frac{d}{dz} \left(\rho D_i \frac{d\omega_i}{dz} \right) - \rho U_s \left(\frac{d\omega_i}{dz} \right) = 0 \quad (5)$$

If the particle dispersion coefficient is assumed to be constant, the above equation can be written as,

$$D_i \frac{d}{dz} \left(\rho \frac{d\omega_i}{dz} \right) - \rho U_s \left(\frac{d\omega_i}{dz} \right) = 0 \quad (6)$$

Data Analysis

The experimental data used in the present analysis were obtained at the ORNL by the research group of Dr. Timothy C. Scott and Mr. John Cosgrove. They recorded the pressure drop along the bed height in a liquid fluidized bed containing 44-53 micron and 63-75 micron coal particles at six different flow rates. The pressure drop vs. bed height data was converted into the total particle concentration vs. bed height data using the following formula

$$(1-\epsilon) = - \frac{dp}{dh} \left(\frac{1}{(\rho_s - \rho_f)g} \right) \quad (7)$$

where, ϵ is the bed void fraction, ρ_s is the density of the solid coal particles, ρ_f is the density of the fluidizing liquid, g is the acceleration due to gravity and dp/dh is the pressure drop along the bed height.

Results and Discussion

The comparison of the experimental data with the model predictions is shown in Figures 4.7-4.12. The absence of any curvature in the model prediction shows that the primary mechanism of the mass transport in the bed is the dispersion of the coal particles. This could be attributed to the fact that the two particle samples used here are of close size fractions. The large particles when carried to the upper regions of the bed as a result of dispersion show a downward or negative segregation velocity. On the other hand, the small particles present in the lower bed regions tend to show an upward or positive segregation velocity. This renders the over-all segregation flux of much less magnitude than the dispersion flux in the present case.

Particle Size Distribution Analysis

Particle size distribution analysis was carried out for five different Illinois No.6 coal samples as obtained from ORNL. These were of the following sieve fractions; 44-53, 53-63, 63-75, 88-125, 125-150 microns. The equipment used for this purpose was HORIBA CAPA-700 Particle

Fig. 4.7

Fig. 4.8

Fig. 4.9

Fig. 4.10

Fig. 4.11

Fig. 4.12

Size Distribution Analyzer which is designed to measure the particle size distribution of particulate samples using a non-contact measuring method based on liquid phase sedimentation. It records the change in the particle concentration during sedimentation using a light transmission method. Both gravity sedimentation and centrifugal sedimentation could be used for this purpose.

Methodology

The preparation of the sample for the size distribution analysis consisted of dispersing the coal sample in a dispersion medium. In order to ensure no agglomeration of coal particles, 0.1% Micro Cleaning Solution from Cole-Parmer was added to the dispersion medium which was either water or a water-glycerol solution depending upon the coal sample being analyzed. The water-glycerol solution helped to control the density and viscosity of the dispersion medium. This was important for obtaining reproducible results especially for coal samples of larger particle diameter which settled very fast in low density and viscosity dispersion mediums. Distilled water was used for coal sample of 44-53 micron sieve fraction. For 53-63 micron coal sample, 40% glycerol solution was used. Other larger size fractions of coal were analyzed in a 60% glycerol solution.

In order to ensure the accuracy of size distribution analysis, the viscosity and density of the dispersion medium was measured in our laboratory. Viscosity was measured in a controlled temperature bath using Schott Gerate Capillary Viscometer. Excellent agreement was found with the reported values in the literature. The particle density was also measured for two different coal fractions; 44-53 and 200-300 micron. It was found to be 1.303 g/cm^3 for the large size fraction and 1.292 g/cm^3 for the small size fraction. In the present size distribution analysis, an average value of 1.30 g/cm^3 was used for all the five size fractions.

The results of the centrifugal sedimentation were found more reproducible while the data obtained from gravity sedimentation showed more scattering. The former method was, therefore, used for the present analysis of all the five coal samples.

The fractional size distribution and cumulative size distribution of all the five coal samples are shown in the Figures 4.13-4.17. It is clear from Figures 4.16 and 4.17 that the reported sieve fraction does not correspond to the particle size distribution analysis.

Fig. 4.13 Sieve Fraction 44-53 micron

Fig. 4.14 Sieve Fraction 53-63 microns

Fig. 4.15: Sieve Fraction 63-75 microns

Fig. 4.16.: Sieve Fraction 88-125 microns

Fig. 4.17: Sieve Fraction 125-150 microns

4.3 BIOCONVERSION OF COAL

C. D. Scott

INTRODUCTION

This program has examined the feasibility of using biological catalysts for the conversion of coal to useful liquid fuels and the biological enhancement of coal derived liquids. 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 chemical modification of enzymes in organic media to enhance liquefaction/solubilization of coal.

Coal Liquefaction/Solubilization Tests

The chemical modification of hydrogenase from *proteus vulgaris* and cytochrome c with dinitrofluorobenzene (DNFB) was reported in Section 4.1. These modified enzymes with dinitrophenyl (DNP) groups were used in benzene or pyridine to convert coal to liquids.

Tests were carried out in shake flasks or in a small fluidized-bed bioreactor.

Tests in Shake Flasks

It was previously shown that the most significant enhancement of coal conversion occurred when both DNP-hydrogenase and DNP-cytochrome c were present in the organic solvent. This mixture was used in all tests describe here. The inclusion of the modified enzymes in the organic liquid reaction mixture clearly enhances the bioconversion of both lignite and bituminous coals. Since the included enzymes may precipitate during the solubilization test or adsorb to the surface of coal residue particles, it has been very difficult to achieve a good material balance based solely on the weights of the coal introduced and the solid residues after the test, especially with the less polar solvents such as pyridine. However, where there was apparent significant precipitation, it was found that treatment of the solid residue with HCl will remove much of the proteinaceous material by hydrolysis with much smaller effects on the coal (Table 4.1). This technique was used in some of the tests.

In most experiments, the increase in light absorbance of the interacting liquid mixture was used as an indication of coal conversion. However, it may be possible that there can be some spectral changes resulting from enzyme variation irrespective of the presence of coal. As shown in Figure 4.18, light absorbance at 280 nm, did increase for mixed enzymes in benzene in the absence of coal indicating some chemical modification of the DNP-enzymes in the organic solvent, but there was an even greater increase in the absorbance at this wavelength when coal was being liquefied/solubilized. This spectral approach should give a useful qualitative indication of coal interaction. In these tests, carried out at 30°C for 24 h, conversion of the bituminous coal was 3.4% in benzene alone and 19.7% when the modified mixed-enzymes were included. It was also shown that a precipitate formed in the benzene-mixed-enzymes solution even in the absence of coal (4.7 mg from an original 9.3 mg of the modified enzymes) even after extensive washing with benzene, acetone, and water. This would result in an erroneously high value for the coal residue when the enzymes were present. When this quantity of precipitated enzymes was subtracted from the residue resulting from the enzyme-coal test, then 29.6% of the coal would have been converted.

Table 4.1. Effects of HCl Treatment on Proteinaceous Residues and Coal^a

MATERIAL	HCl Concentration (N)	Temperature (°C)	Time of Contact (h)	Solubilization (%)
Cytochrome Precipitate	0.5	60	1.0	68
	2.0	60	1.5	69
	2.0	60	12.0	71
Hydrogenase Precipitate	0.5	60	1.0	73
	2.0	60	1.5	83
Mixed Enzyme Precipitate	2.0	60	0.5	80
Bituminous Coal	0.5	60	1.0	5.5
	2.0	60	0.5	4.8
	2.0	80	12.0	8.5

^aTests were made in 25 mL shake flasks immersed in a temperature-controlled water bath in contact with air. Approximately 50 to 100 mg of the precipitate was contacted with 10 mL of the aqueous solution.

Fig. 4.18. Enhanced liquefaction of bituminous coal by a mixture of 0.6 mg/mL DNP-hydrogenase and 0.3 mg/mL cytochrome c in benzene at 30°C in a shake flask under H₂ compared to benzene alone and benzene with 0.5 mg/mL of DNP-albumin.

There was also concern that there may be a noncatalytic biological effect on coal solubilization perhaps due to the surfactant properties of proteins. In order to test this hypothesis, chemically-modified albumin, a noncatalytic enzyme, was also used in benzene in contact with bituminous coal. In this case, the protein had no apparent effect either from an increase in the absorbance of the reaction mixture (Figure 4.18) or the amount of coal conversion (3.1% vs. 3.4%) when compared with benzene alone. Thus, the dominant enhancement of coal conversion appears to be from the biocatalytic effects of the DNP-mixed enzymes.

Since cytochrome c in the reduced state is an excellent reducing agent, it is likely that it serves this purpose in the hydrogenation of coal. Hydrogen gas was also present as the possible reducing agent. In order to determine the relative effects of these two types of reducing substances and to also study pyridine as the organic solvent, tests were made in which a H₂ atmosphere was compared with a N₂ atmosphere in the enzymatic interaction with bituminous coal at 30°C for 24 h (Figure 4.19). It was found that the enzymes did increase coal conversion and that the effects were apparent in the absence of H₂, although there was

an additional enhancement when molecular H_2 was also present. This indicates that both a dissolved reducing agent and molecular H_2 can be used by the biocatalyst.

There appeared to be an even greater amount of enzyme precipitation occurring in pyridine probably due to the larger quantity of dissolved enzymes in this solvent. This material was observed as a light brown fluffy material mixed with the more granular coal residue particles. A series of shake-flask tests were made at $30^\circ C$ under H_2 for 24 h in which bituminous coal was contacted with pyridine alone, with pyridine containing 6.2 mg/mL DNP-albumin, and with pyridine containing 4.1 mg/mL DNP-hydrogenase and 6.2 mg/mL DNP-cytochrome c. After treatment of the residues with 2N HCl for 0.5 h at 60° and subtracting out the expected amount of coal solubilization from the acid treatment (Table 4.1), 10.8% of the coal was converted in the presence of the DNP-mixed enzymes compared to 6.1% for pyridine alone and 6.5% when the DNP-albumin was present. This was clearly an enhancement by the mixed enzymes, but since this degree of coal conversion is less than that seen with the use of benzene, this might indicate that the less polar solvent is superior.

Fig. 4.19. The comparison of enzyme-enhanced bioconversion of bituminous coal in pyridine at $30^\circ C$ under a N_2 or H_2 atmosphere in shake flasks. A mixture of approximately 2 mg/mL of NDP-hydrogenase and 4 mg/mL of NDP-cytochrome c was used and compared with reference tests that included no enzymes.

Enzyme-enhanced solubilization of North Dakota lignite in pyridine was also studied in shake-flask tests. As with the higher rank coal, mixed enzymes in the organic solvent also enhanced the bioconversion of this type of coal with 7.8% of the coal being converted in pyridine alone and 15.4% being converted when the DNP-mixed enzymes were included during the course of 24 h at 30°C under a hydrogen atmosphere.

Tests in Fluidized Beds

Coal conversion tests in a small fluidized-bed bioreactor represent a more realistic environment for possible process applications. Two types of tests were made: one in which the initial charge was maintained throughout the test with periodic measurements of spectrophotometric changes in the organic solution; and a second type in which the solvent with modified enzymes was periodically replenished while the coal residue was maintained in the reactor. The latter type of test was somewhat representative of a continuous system in which some fresh biocatalyst was continuously introduced. Although earlier tests of this type were made with bituminous coal in benzene, these current tests were made with pyridine as the solvent in contact with either bituminous or lignite coal.

Typically, the results from fluidized-bed tests with a single charge of the solvent containing DNP-enzymes had trends similar to those observed in the shake-flasks experiments. That is, an apparent rapid conversion of the coal during the first few hours followed by a more gradual process throughout the remaining 24 h (Figure 4.20). This is quite similar to that observed in shake-flask tests and could be due to an initial use of the included reducing agent (DNP-cytochrome c) for the hydrogenation reaction followed by the use of molecular H₂ for the succeeding hydrogenation at a lower rate. Without treatment for removing enzyme precipitation, the liquefaction/solubilization of the lignite was 23.9% and of bituminous coal was 8.5%. This was somewhat higher than the comparable shake-flask tests for both types of coal without HCl treatment. This seems to indicate that the fluidized bed is a more efficient contacting system.

One test was made with bituminous coal in pyridine in which the solvent containing DNP-mixed enzymes was replaced after 4 and 8 h in order to determine if appreciable interaction could be induced throughout the course of the 24-h run (Figure 4.21). This was apparently the case since there was a significant increase in absorbance at 376 nm throughout

Fig. 4.20. The conversion of lignite and bituminous coals in the small fluidized-bed bioreactors in pyridine at 30°C under H_2 and enhanced with mixed DNP-enzymes. The DNP-hydrogenase concentrations were 4 mg/mL and 6 mg/mL for the lignite and bituminous tests, respectively, and DNP-cytochrome c concentration was 3 mg/mL for both experiments.

Fig. 4.21. The conversion of bituminous coal in the small fluidized-bed bioreactor in pyridine at 30°C under H_2 and enhanced with mixed DNP-enzymes. DNP-hydrogenase concentration was 4 mg/mL, and DNP-cytochrome c concentration was 3 mg/mL. Approximately 95% of the solvent mixture was replaced with fresh solutions at 4 and 8 hours.

a greater portion of the 24-h test. Apparent coal conversion without acid leaching of the residue to remove precipitated enzymes was 35.3%. This is the largest amount of biocatalyzed liquefaction/solubilization of a higher rank coal that has been observed and it is a three-fold increase over the fluidized-bed in which there was a single charge of the solvent mixture.

Product Characterization

As would be expected, the particle size distribution of the coal changed as conversion occurred. With the bituminous coal, the larger particles appeared to diminish in size, and many of the very small particles tended to disappear (Figure 4.22). This would indicate that the enzyme-catalyzed process occurred only on the outer surface and even smaller particles would be more effective.

Fig. 4.22. Cumulative distribution of bituminous coal particle size before and after conversion in the small fluidized-bed bioreactor containing pyridine with DNP-mixed enzymes at 30°C for 24 h.

As previously shown, the liquid product from the hydrogenase-enhanced conversion of bituminous coal in benzene had a volatility in which greater than 60% of the material had a boiling point of less than 280°C. The liquid product of the mixed-enzyme-enhanced liquefaction of bituminous coal in pyridine was somewhat less volatile with greater than 55% of the solutes having a boiling point less than 280°C. That material was also more polar than the product from benzene with 17% being extracted in an equal volume of water in contact with the product and benzene.

The bioconversion product from lignite was different with only 50% of the material having a boiling point less than 280°C. Also, about 25% of this material had precipitated in the pyridine and was soluble in water. This water-soluble material was somewhat similar to the products obtained by aerobic microbial interaction with the same type of lignite. Thus, this material probably also included higher-molecular-weight coal fragments with a significant amount of oxygen remaining in the structure.

4.4 MILD GASIFICATION PRODUCT CHARACTERIZATION

R. L. Graves

INTRODUCTION

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.

Project Status

The Cooperative Research and Development Agreement (CRADA) with B&W has been completed. The subject of the CRADA is the characterization of the basic combustion properties of char. Stuart Daw expects to travel to B&W to resume work on characterizing chars obtained last year from some of the mild gasification teams. B&W provides technical effort and funds to extend the characterization work to study char combustion under pressurized fluidized bed conditions.

Coal Technology Corporation (CTC) representatives visited ORNL during this reporting to discuss the feasibility of using our dilute alkali extraction technology to convert some of their highly aromatic middle distillates to useful products. As mentioned in a previous report, we began examining how to derive useful fuel material from the caustic wash of the mild gasification liquids. Recall that about two-thirds of the total liquid was extracted by the caustic wash. While this greatly improved the quality of the remaining diesel-fuel-like material, it gives at least the appearance of a greatly diminished yield of useful liquids from mild gasification. To reduce emulsion formation and viscosity during caustic washing of mild gasification middle distillate liquids, we used pentane as a volume/volume hydrocarbon diluent and extracted with 1 N, rather than 50%, NaOH. After extraction, we removed the pentane by rotary evaporation to produce a coal diesel fuel. We felt that pentane was a good model compound for the light ends produced in mild gasification. We then acidified the mild caustic wash and extracted it several times with a total of one volume of toluene. The samples of coal liquid that their researcher brought with him were simply too heavy and viscous for a successful extraction. However, we were able to instruct him on the extraction technique and we suggested that they operate their reactor at a lower temperature to improve the quality of the liquid product. Subsequently, CTC has performed trial extractions at their site which apparently were successful on lighter liquid samples they have been able to produce. Once a satisfactory sample of extracted material is available, we will conduct an evaluation of its ignition quality in a diesel engine.

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5. COAL COMBUSTION RESEARCH

R. L. Graves

5.1 ANALYSIS OF FBC DETERMINISTIC CHAOS

C.S. Daw

INTRODUCTION

Unique and innovative approaches are needed to optimize fossil energy conversion processes (such as fluidized bed combustion, coal gasification, hot-gas cleanup, oil-shale retorting, catalytic cracking of petroleum, and coal slurry combustion) that involve the intimate contacting of gases and particulate solids. Of particular concern is the need to develop improved diagnostics for preventive maintenance, scale-up and engineering design procedures, and process control methods to maximize performance and minimize emissions.

Recent research suggests that much of the conventional dynamical theory used to characterize and model fossil energy processes involving multi-phase flow and gas-solids contacting is inadequate to describe the nonlinear components in these systems. Further, analysis of many commonplace phenomena involved in fossil energy systems (such as fluid turbulence and chemical reactions) suggests that nonlinear processes are the rule rather than the exception. Such nonlinearities frequently are the cause of behavior that appears highly irregular and complex, at least on the surface. This behavior has been labeled "deterministic chaos" or just "chaos" for short. Data from laboratory-scale simulations of fossil energy conversion processes have already been used to demonstrate the presence of chaos in these processes.

Status Summary

Activity during this reporting period focused on follow-up to the fluidized bed data analyses and modeling initiated previously and on developing new activities in the application of chaos theory to pulsed combustion.

Fluidized Beds

As described previously, pressure and voidage data are being routinely acquired from laboratory fluidized beds at ORNL, the University of Tennessee, and Morgantown Energy Technology Center. The fluidized bed facilities at the University of Tennessee have been expanded to include a 14- cm-diameter straight-walled bed and a 15.2-cm nominal diameter tapered bed. In addition, pressure-drop data have also obtained from fluidized bed test facilities operated by MIT, Cornell University, Babcock and Wilcox, and Foster Wheeler Corporation. We are working with the above organizations and other fluidized bed research centers to establish clear standards for data collection and analysis.

All fluidized bed data collected is evaluated in terms of the phase-space signatures described in the previous report. Our objective is to identify characteristic features that can be used as diagnostic indicators of fluidization regime and/or desirable and undesirable performance (e.g., good mixing, poor mixing). We are also investigating phase-space signatures as a basis for developing on-line control systems. As a result of related activities being conducted for the Oak Ridge Y-12 Plant, a prototype fluidization monitor and controller have been built and demonstrated. The latter device is based directly on the application of the phase-space signature concept.

A paper summarizing the previously reported bubble growth model for fluidized bed "chaos" was presented at the AIChE National Meeting in Los Angeles last November. This paper has been selected for inclusion in the 1992 AIChE Symposium Series, Fluidized Processes: Theory and Practice.¹ It is anticipated that future work on this model will include the addition of gas flow perturbations and control models to investigate the potential for inducing novel fluidization states.

Pulsed Combustion

The intense acoustic energy generated by unsteady combustion promises benefits to a number of advanced fossil energy applications.² In conjunction with ongoing research at METC in pulsed combustion of fuel gas and coal slurries we have begun investigating the potential for chaotic behavior in pulsed combustion. Our initial efforts have focused on the computer modeling of a particular version of pulsed combustion developed at METC and known as "thermal pulsed" combustion. This particular version of pulsed combustion is

unique in that it involves a continuously mixed, jet-stirred combustion chamber with a steady supply of air and fuel with no mechanical or aerodynamic valves.

The computer model has revealed a surprising variety of behavior including clear regions of chaos for certain values of the operating parameters. This observation is especially important because it demonstrates that chaotic behavior can occur during combustion as a result of nonlinear interactions between simple heat, mass, and momentum balances that are independent of fluid turbulence (i.e., the interactions occur under simplifying assumptions where fluid turbulence is not present). This suggests that some level of chaos may be present in many types of combustion (not just pulsed combustion). Perhaps even more importantly, the characteristic irregular fluctuations associated with chaos may have an impact on the transient formation of undesirable emissions such as NO_x.

A short paper summarizing our initial results on pulsed combustion will be presented at the 1992 Technical Meeting of the Central States Section of the Combustion Institute this April.³ Analyses of experimental pulsed combustor data from METC and more in-depth modeling studies are planned.

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5.2 TECHNICAL SUPPORT TO PETC-USAID COLLABORATIVE COAL PROJECTS

R. P. Krishnan

INTRODUCTION

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.

Background

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 in the following projects.

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/SO_2 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/SO_2 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/SO_2 emissions; and (4) simulation and modeling of the combustion and heat-transfer processes in the boiler for NO_x/SO_2 prediction.

The BHEL, Trichy, will carry out the projects in India as part of their ongoing research and development on NO_x/SO_2 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/SO_2 measurement, and training of the BHEL engineers in selected U.S. utilities (TVA and others) on NO_x/SO_2 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.

Status Summary

During this reporting period, the activities and accomplishments in each of the five coal projects are summarized below.

Project 1. The emissions monitoring was conducted at the Vijayawada Thermal Power Station (VTPS) in Vijayawada, India, 600 km north of Madras. Coordination and planning for the test program was done jointly by BHEL, the Central Power Research Institute (CPRI), Bangalore, the Tennessee Valley Authority (TVA), and ORNL. The test matrix was

finalized on February 2-3, 1992, and the monitoring at the site was completed between February 6-10.

The present installed capacity of the thermal station is 840 MW which is generated by four BHEL supplied, Combustion Engineering (CE), USA designed, 210-MW tangential fired boilers. The boilers are two pass, radiant reheat, balanced draft and natural circulation units. The four boilers are housed in two adjacent bays. Stage 1 has two units and the remaining two units are housed in Stage 2. Stage 3 with two more 210-MW units is under construction. Stage 3 boilers will be single pass, tower type and will also be supplied by BHEL in collaboration with Stein Industries, France.

Average plant availability for VTSP is above 90 percent which is a record in the country. The national average is only 60 percent. The cleanliness and overall housekeeping throughout the plant were impressive and comparable to some of the best U.S. power plants. The plant operators were particularly receptive to the special demands of the sampling team and ensured that the test conditions were maintained during the sampling period. The plant operates on a three shift cycle, seven days a week. The monitoring was conducted in one of the Stage 1, 210-MW boilers. The sampling point was located in the flue gas duct downstream of the ESP.

Equipment for the stack gas monitoring was provided by BHEL, CPRI, TVA, and PETC. A total of twelve tests were conducted. In six of the tests, the conditions simulating overfire air operation were maintained. In all the twelve tests, the boiler load was maintained at near full load (210-MW), with the bottom five coal mills (Mills A through E) in continuous operation and zero burner tilt. Mill F at the uppermost elevation was not operated in the coal feeding mode. The ports were kept closed except during testing with overfire air.

Excess air control was done manually in the control room. Maintaining the excess air within the set band posed difficulties because of coal quality variations. The drift was +0.5 percent and in some cases as high as +1 percent. The boiler load was held constant at 210-MW. However, this became difficult towards the end of the test program because the coal reserve in the plant was shrinking and fresh coal had not arrived at the site. The plant operators were forced to drop load to conserve coal and continue to keep the plant running.

The test results are given in Table 5.2.1. A summary of the NO_x/SO_2 emissions, and a set of typical boiler operational data are given in Table 5.2.2 and 5.2.3, respectively. The

Table 5.2.1. VTPS-Unit 1 Stack Pollution Monitoring Test Results

Test No.	F&FF Dampers*	Excess Air	Fuel Air Damper	LOAD (MW)	CO (ppm)	NO _x ppm @ 3% O ₂	SO ₂ (lb/10 ⁶ Btu)**	NO _x (lb/10 ⁶ Btu)**	SO ₂ (lb/10 ⁶ Btu)**
1	closed	20%	normal	204	126	310	502	0.42	0.95
2	closed	20%	5% open	210	91	259	723	0.35	1.37
3	closed	25%	normal	211	125	303	681	0.41	1.29
4	closed	25%	5% open	182	153	229	679	0.31	1.29
5	closed	15%	normal	184	170	248	621	0.34	1.18
6	closed	15%	5% open	182	95	185	632	0.25	1.20
7	open	20%	normal	210	120	184	578	0.25	1.10
8	open	20%	5% open	204	101	171	565	0.23	1.07
9	open	25%	normal	190	99	262	-	0.36	-
10	open	25%	5% open	185	102	222	485	0.30	0.92
11	open	15%	normal	181	81	214	497	0.29	0.94
12	open	15%	5% open	185	53	205	493	0.28	0.93
13	closed	20%	normal	172	139	225	650	0.31	1.23

*Dampers associated with coal mill F.

- Two sets of control room readings taken; first set after 30 to 60 minutes of stabilized operation of the boiler; next set after 15 minutes interval.
- Gas analyzer reading taken at 5 minutes interval, 30 to 60 minutes after stabilized operation of the boiler.
- Raw coal samples collected from the coal feeders A, C and E, one per test and composite sample made by Quarter Cone Method
- Flyash samples collected from first three fields of Stream-C1
- Three sets of coal samples analyzed for coal fineness

**Calculated based on USEPA emission factor.

Table 5.2.2. SUMMARY OF NO_x/SO₂ EMISSIONS AT VTPS

NO_x Emission (pounds/million Btu Heat Input)

	F & FF closed			F & FF open		
	Excess Air 25%	Excess Air 20%	Excess Air 15%	Excess Air 25%	Excess Air 20%	Excess Air 15%
Fuel air damper	0.41	0.42	0.34	0.36	0.25	0.29
Open	{211}	{204}	{184}	{190}	{210}	{181}
Fuel air damper	0.31	0.35	0.25	0.30	0.23	0.28
Closed	{182}	{210}	{182}	{185}	{204}	{185}

The Boiler Load in MW are given within brackets.

SO₂ Emission (pounds/million Btu heat input)

	(Excess Air)			(Excess Air)		
	25%	20%	15%	25%	20%	15%
Fuel air damper	1.30	0.94	1.18	-	1.10	0.91
Open						
Fuel air damper	1.29	1.40	1.20	0.92	1.10	0.93
Closed						

Table 5.2.3. Typical Boiler Operational Data

Stack Polution Monitoring
Vijayawada TPS, Unit-1

Date	7/2/92		
Start time	12:00		
Read time	13:00		
Load-204 MW			
F&FF Dampers-Closed			
Damper Behind Fuel-Normal			
Excess Air-20%			
SH Out Flow	t/h	605	Secondary Air Damper Positions
SH Out Pr	kg/sqcm	132	
SH Out T	deg C	532.5	
Sh Spray	t/h	4	<u>Damper % open</u>
RH Spray	t/h	1.5	FF zero
Feed Water Flow	t/h	670	F zero
Burner Tilt	deg	-19	EF 13
ECO Out O2	%	3.4	E 25
Pry Air Flow	t/h	270	DE 13
Secy Air Flow	t/h	520	D 25
Secy Air T	deg C	327	CD 13
Furnance Pr	mmwc	-10	C 30
Wind Box Pr	mmwc	60	BC 13
RH Out Stm T	deg C		B 40
ECO In Water T	deg C	250	AB 13
ECO Out Water T	deg C	300	A 50
FD Fan Out T	deg C	36	AA 100
AH Out Pry Air T	deg C	308	
AH Out Secy Air T	deg C	327	
ECO In Gas T	deg C	430	
AH In Gas T	deg C	363	
AH Out Gas T	deg C	181	

MILL	Feeder Speed rpm	Pry Air Flow t/h	Mill Out Temp deg C	Motor Current Amps
A	35	50	75	33
B	25	55	73	36
C	20	46	70	35
D	22	54	75	36
E	24	53	68	36
F	-	-	-	-

measured values are given in parts per million (ppm) and the calculated NO_x/SO₂ emissions are given in pounds per million BTU (lbs/10⁶ Btu). These are preliminary estimates obtained using the USEPA recommended emission factors. The final numbers will be available once the fuel and ash analyses are completed. From the preliminary results, the NO_x emissions appear to be within the USEPA allowable limits of 0.6 lbs NO_x/million Btu. SO₂ is borderline and in many tests exceeds the USEPA limits (1.2 lbs SO₂/million Btu).

Overfire air tends to reduce the NO_x levels, as expected. As an illustration, at 20 percent excess air, the NO_x emissions (170 ppm) was about one-half compared to the NO_x emissions in the test without overfire at the same excess air level. Increasing the excess air increased NO_x but the effect was not as pronounced as expected. An interim report was prepared at the site after the tests were completed.

Project 2. The modifications recommended to the existing SCC at Trichy by PETC and the USDOE contractors during the visit of two BHEL engineers in July-August 1991, are being implemented at Trichy. The slag port has been enlarged and the installation of the heating system for the slag port is in progress. Changes to the coal feed system have been completed. The performance of the new coal feed system will be tested in June 1992 after the heating system for the slag port has been installed. The other recommended modification was to enlarge the optical port for flow visualization. This will not be possible due to physical constraints in the existing combustor. The conceptual design of the second version of the SCC, which was also recommended, is in progress. This version will feature double tangential entry of air into the combustor as contrasted to the present single entry system. Detailed engineering and the fabrication will be done in Trichy in consultation with PETC and ORNL. All the USAID supplied equipment for this project has already arrived at the site. The only remaining activity is to provide two weeks of on-site technical assistance to BHEL when the combustor is ready for restart and shakedown operations.

Project 3. The major engineering design of the FETF, test facility layout, structural design and equipment specifications were completed in earlier visits of ORNL and PETC to Trichy. Ground breaking for the FETF was performed in September 1991 and since then the construction and fabrication of components have been in progress at the site. The USAID equipment for the FETF was shipped in two consignments from PETC in January-February 1992 and have reached the site. Dr. N. Stanley Harding, Vice President, Reaction Engineering, Inc., Pittsburgh, left for Trichy on January 23, 1992, with the R. P. Krishnan

to finalize the pending design related issues. Dr. Harding spent two weeks in Trichy (January 23-February 7, 1992) with BHEL to resolve the issues.

All the control and instrumentation drawings for the coal handling, primary, secondary and compressed air, the Dowtherm cooling system, demineralized and soft water system, fouling probe and the flue gas recirculation system were reviewed, updated and finalized.

Modifications to the furnace assembly to include a bottom ash hopper and consolidation of all view ports, sample and heat flux measurement ports, and soot blower ports onto one side of the furnace were recommended. The nose and inlet to the convection section have been modified to conform to Indian utility boilers. The radiant section of the furnace will be assembled in pieces and will consist of the ash hopper, the firebox, two radiant sections and the nose. This will facilitate repairs in the firebox section.

The previously contemplated 1.5 MM Btu/h wall-fired oil burner was rejected. Instead, it was decided to go with four smaller burners, 750,000 Btu/h each, two on the front wall and two on the rear wall. Ultraviolet flame scanners have also been recommended to detect both oil and coal flames.

The slag panel system will consist of two slag panels, 200 x 300 mm, and one larger slag panel, 600 x 1020 mm, cooled by Dowtherm to remove up to 1.0 MM Btu/h and multiple water cooled panels to remove an additional 0.5 MM Btu/h. The Dowtherm cooled slag panels will be commercial plate coils and the water cooled panels will be fabricated by BHEL. A spare Dowtherm pump and an emergency generator for safety have been recommended. An air-cooled radiator designed to remove 1.0 MM Btu/h heat from the Dowtherm will be installed.

A bank of fouling probes, two in the entrance to the convection section (1200°C to 1093°C), and one at the outlet of the first convection pass, will be installed. The typical velocity in these probes will be 18 m/s and the skin temperature will correspond to commercial boilers.

To test corrosion and erosion, it is proposed to use test metal coupons of platinum/tin substrate material. Ultrasonic thickness measurement will be used to estimate metal wastage.

Dr. Harding agreed to provide the typical procedures for curing of refractory, startup and operation procedures and the typical measurements to be made during the tests. He also

made a highly appreciated presentation on "Coal Quality Effects on Power Plant Performance--Application of Pilot-Scale Data and Modeling" to an audience of 50 senior executives of BHEL, Trichy. In his presentation, Dr. Harding discussed at length how to extrapolate the data from the FETF to predict trends in combustion efficiency, emissions, heat absorption in the furnace and other important combustion performance indicators in commercial boilers.

The traveler had one more opportunity to discuss the FETF after Dr. Harding's departure. All the necessary input for the design and the instrumentation associated with the main furnace are now available at BHEL to complete the fabrication of the furnace and auxiliary systems. The civil works (laying of foundation, structures, and construction of the control room) will be completed in April 1992. Sixty percent of the components have been fabricated and the remaining 40 percent will be completed in April 1992. The electrical power supply system to the FETF will be completed about the same time. Procurement action for the indigenous items from local vendors has been initiated. However, this is an area where BHEL will have little control on the delivery time. It is expected that by August-September 1992 all indigenous equipment, including the instrumentation and control system panel, will be on site. Erection will start immediately and is scheduled for completion in two months. Commissioning of the test facility will not be until December 1992, six months beyond the scheduled completion date.

Mr. A. V. Narayanan, General Manager, BHEL, Trichy, has written to GOI and USAID explaining the delay in the FETF schedule and requesting PETC and ORNLs assistance to complete the project. Many extraneous factors have contributed to the delay. The recent fiscal policy changes in GOI, denial of custom duty waiver for the USAID supplied equipment and the devaluation of the Indian rupee slowed down the progress. The situation is now under control. An additional \$150 K from USAID will be required to complete the FETF.

Project 4. Four U.S. experts visited India during February 10 through March 5, 1992, to participate in a joint life assessment demonstration with BHEL. The scope of the assessment was restricted to the boiler, boiler internals, headers, steam lines, piping and support structures. The assessment was conducted at the Nasik Thermal Power Station (NTPS) in Nasik, India, 200 miles east of Bombay. The U.S. team members were:

1. Mr. Blain Roberts, Tennessee Valley Authority, Chattanooga, Tennessee; 2. Mr. Lany Bisbee, Failure Analysis Associates (FAA), Alexandria, Virginia; 3. Mr. Marvin Cohn, Aptech Engineering Services, Sunnyvale, California; and 4. Mr. Eric Sullivan, Aptech Engineering Services, Sunnyvale, California.

Dr. William Peters, PETC, and Dr. R. P. Krishnan, ORNL, participated in the demonstration. Mr. Robert Blumberg and Mr. N. V. Seshadri, from USAID, New Delhi, visited the site during this period. Unit No. 2 of the Nasik thermal power station (NTPS), owned and operated by the Maharashtra State Electricity Board (MSEB), was shut down on February 11, 1992, to conduct the assessment.

Unit No. 2 had operated for 153,000 hours since commissioning in March 1971. Acid cleaning of the boiler was done in 1990. There had been repeated failures in the primary superheater coils, reheater inlet and outlet stub welds, and tube thinning in the economizer section due to gas side erosion. Presently, the boiler operates at a load of only 95 MW with low hot reheat temperature of about 520°C. The design conditions are 140 MW and 540°C reheat temperature. Maximum continuous rating of the unit is 400 T/h steam at 145 kg/cm² and 540°C. MSEB awarded a contract to BHEL to conduct a life assessment study on this boiler.

The boiler is a balanced draft, natural circulation, two pass, dry bottom design supplied by Babcock and Wilcox, France. Four B&W EM 90 type coal mills feed at four elevations to the sixteen burners located in the front wall of the boiler.

The superheater section consists of a primary superheater located in the second pass. The secondary radiant superheater and the convection superheater are of pendant design. Superheat temperature control is achieved by water injection. The location of the injection nozzle is between the primary superheater outlet and the secondary radiant superheater inlet.

The reheater is of pendant design with a cross-flow arrangement. Reheat steam temperature control is primarily by gas recirculation. Water injection is used only in the event of disturbed operation. Soot blowers of the retractable type are provided in the furnace and long retract blowers are provided in the superheater and reheater sections. An ESP is provided at the air heater outlet for particulate emissions control. The air heater is a Ljungstrom regenerative type.

The design coal is 9 percent moisture, 20 percent ash, 22 percent volatile matter and 5800 kcal/kg higher heating value (HHV). However, the coal burned in the plant is almost

40 percent ash and only 3400-3800 kcal/kg HHV. Higher ash content and the lower heating value are mainly responsible for almost all the operational problems in the plant.

The flue gas temperature leaving the boiler is around 160°C which is higher than the design temperature. Soot blowing is done by the wall blowers once in each shift, typically at 8 h intervals. The long retractable blowers are operated twice a week.

The life assessment team arrived at the site on February 13, 1992. BHEL team members were already at the site preparing for the assessment. A hot inspection of the piping and piping supports was conducted prior to the shutdown. Detailed discussions were held with the plant personnel followed by a thorough walkdown inspection. After this, the components to be inspected, the schedule for inspection, and the groups responsible for the inspection were identified. Table 5.2.4 lists the components inspected and the techniques used for inspection. ORNL and FAA had arranged for the necessary equipment from the U.S. to be shipped to the site. A list of this equipment is provided in Table 5.2.5.

Tube samples were taken from selected locations in the waterwall, economizer, primary, and secondary superheater and reheater sections. These were shipped to the laboratories at Trichy for analysis of internal deposits/scales and for microstructure examination. Coal samples and deposit samples collected were also sent to Trichy. Results are pending and will be presented in the final report.

The salient observations from the condition assessment were:

- Heavy deposition was seen in the furnace and in the secondary superheater zone.
- Bowing and distortion of the 17th and 18th assemblies of secondary superheater had occurred. Most of the spacers were also found cracked and/or detached.
- All hangers in the piping were found to be loaded within the range except a few in the main steam line at the turbine end. Detailed stress analysis has not been completed to recommend corrective action.
- The seal plate weld on the main steam pipe on the penthouse wall was found cracked. However, this is not a serious problem. Corrective measures required will be communicated to MSEB after the main steam line hanger analysis is completed.
- Severe erosion was observed around the tube welds in the primary superheater inlet header top surface. A minimum of 28.3 mm was measured against the nominal thickness of 42.0 mm.

**Table 5.2.4. Components Checked and Assessment Techniques
Adopted in NTPS Unit No. 2 Life Assessment Study**

No.	Component	Tests Conducted
1	Drum	Visual inspection Penetrant testing Ultrasonic testing of circumferential and longitudinal welds and magnetic particle testing on downcomer welds.
2	Water wall tubes	Visual inspection Dimensional check Ultrasonic testing (for hydrogen damage) Metallography Deposit Analysis.
3	Economizer tubes	Visual inspection Dimensional check Macro-examination of tube sample inner surface
4-7	Primary superheater tubes Radiant superheater tubes Convection superheater tubes Reheater tubes	Visual inspection Dimensional check Steam side oxide thickness measurement Metallography Fireside deposit analysis
8	Economizer inlet header	Visual inspection Dimensional check Penetrant testing on stub welds Video borescopic examination of the ligaments and header inside surface.
9	Primary superheater outlet header	Visual inspection Dimensional check Penetrant testing, Magnetic particle testing on stub welds, Ultrasonic testing on girth welds. Replica analysis Video borescopic examination of ligaments and inner surface
10	Desuperheater	Visual inspection Video borescopic examination of the liner and welds.

No.	Component	Tests/Conducted
11	Secondary superheater inlet header	Visual inspection Dimensional check Penetrant testing Magnetic particle testing of stub welds, Ultrasonic testing of girth welds.
12	Secondary superheater outlet header	Visual inspection Dimensional check
13	Reheater inlet header	Penetrant testing
14	Reheater outlet header	Magnetic particle testing of stub welds Ultrasonic testing of girth welds. Replica analysis Video borescopic examination of ligaments and inner surface.
15	Cold reheat spray	Video inspection Video borescopic examination of liner and welds.
16	Main steam piping	Visual inspection
17	Hot reheat piping	Hanger checks Dimensional check Penetrant testing Magnetic particle testing Ultrasonic testing of girth welds and safety valve fillet welds. Replica analysis.
18	Cold reheat piping	Visual inspection Hanger checks Ultrasonic testing of pipe after cold reheat spray.
19	Piping hangers	Visual inspection Physical location measurements
20	Critical supports welded to pressure parts and attachment	Visual inspection Penetrant testing
21	Burners	Visual inspection
22	Soot blowers	Visual inspection
23	Critical ducting	Visual inspection Dimensional check

Table 5.2.5. List of Equipment Provided by Failure Analysis Associates

No.	Equipment
1	Welch Allyn video probe and probe processor
2	Welch Allyn video probe and probe alphanumeric display system
3	Articulating video probes
4	Sharp TV monitor
5	Hitachi VCR tuner
6	Hitachi VCR player
7	Transpol portable mechanical polishing unit
8	Bosch die grinder and accessories
9	Olympus portable microscope and accessories
10	In-situ oxide scale thickness measurement system
11	SSam-2, Remote Computer Controlled, Surface Sampling Device and Associated equipment
12	Camera, microscale, level meters for piping and hanger inspections

- Borescopic examination of the reheater inlet header showed erosion damage in the bore hole and the stub inside surface in a few assemblies on either side of the T-piece.
- Erosion damage was also observed in the cold reheater pipe bend (90° bend) to the reheater inlet header.
- Ligament cracks were seen in the reheater outlet header. However, the cracks were found to be below the detectable limit of ultrasonic equipment.
- The cold reheat spray nozzle showed erosion both at the nozzle and backing plate. The liner at the upstream showed numerous cracks in the liner-to-ring weld and a circumferential crack at the downstream end. The liner is still in place and has not moved.
- Desuperheater showed a small crack at the weld between the liner and the fixing ring.
- The final superheater outlet header had ligament cracks initiated.

- Coal and oil burner components showed severe erosion and cracking.
- Waterwall section in the boiler surveyed for hydrogen embrittlement damage were found acceptable for trouble-free operation.

There were no major damage or indications found in the condition assessment which warranted immediate repair or replacement to the boiler, main steam lines, or piping/support. However, several components need periodic and close monitoring and, in specific instances, replacement at the earliest opportunity has been recommended.

Pending laboratory analysis and stress calculations, the following recommendations were made to MSEB.

- The cold reheat spray should be closely monitored and controlled to avoid erosion in stubs in the reheat inlet header.
- The reheater outlet header may be continued in service but the temperature should be closely monitored by installing thermocouples in the affected ligament zones. Ultrasonic testing during every annual overhaul to detect crack growth and detailed analysis of cracks that have grown to detectable limits are necessary.
- The cold reheat attemperator should be closely monitored and replaced at the earliest opportunity.
- The secondary superheater outlet header, the desuperheater, and the cold reheat pipe bend are to be closely monitored.
- The deposits on the water walls and on the secondary superheater should be thoroughly removed by cleaning.
- The primary superheater inlet header should be shielded to prevent further damage from erosion.

Project 5. There has been no further activity on the project beyond what was reported in the Semi-Annual Report for October 1990 - March 1991. USAID funding for this project terminated in December 1990.

Dr. R. P. Krishnan, ORNL, traveled to India on January 23, 1992 for on-site coordination and assistance in the emissions mounting and life assessment activities. He also participated in a one-day workshop on "Life Assessment of Thermal Power Plants" organized by the Power Finance Corporation (PFC) in New Delhi, on February 27, 1992, along with Dr. W. C. Peters, PETC and the four US experts who traveled to India for the life

assessment demonstration at NTPS. Technical presentations were made by the U.S. participants. Over seventy-five people from the state-owned utilities, the nodal power sector agencies of GOI, equipment manufacturers, consulting and engineering companies and national laboratories attended the workshop. Following the workshop, Dr. R. P. Krishnan had several meetings with PFC. The purpose of these meetings was to assist PFC in preparing a draft implementation plan for the power plant life assessment demonstration model study component under the recently initiated USAID/PFC Energy Management, Consulting and Training (EMCAT) project.

Mr. David Daugherty, and Dr. C. M. Huang, Research and Development, TVA, Chattanooga, attended these meetings between March 9 through March 16, 1992. PFC considers TVA as a valuable resource for this project because of their knowledge and breadth of experience in coal-fired power plants. A preliminary statement of work for the model study has been prepared jointly by PFC, ORNL, and TVA. The work statement is now being reviewed by the PFC management and the USAID, New Delhi. Further details are provided in the trip report of R. P. Krishnan, ORNL/FTR-4210, March 31, 1992.

During the next reporting period the site activities on the FETF will proceed at BHEL, Trichy. ORNL and PETC will continue to provide assistance to BHEL to complete the erection of the test facility. All the joint activities identified under Project 1, 2 and 4 have been completed except for the preparation of the final report.

6. FOSSIL FUEL SUPPLIES MODELING AND RESEARCH

P.N. Leiby

The current fossil fuel supply-related projects assist DOE in addressing policy issues related to strategic fuel reserves, drawdown, and energy security.

6.1 STRATEGIC PETROLEUM RESERVES PLANNING AND MODELING

P. N. Leiby

DISCUSSION OF CURRENT ACTIVITIES

Project work focused on the benefits of increasing the drawdown and distribution capability of the Strategic Petroleum Reserve (SPR). In a study by Trumble and Lee,¹ two models (DISSPR and ORNLTEIS) were used to compute the expected benefits of alternative drawdown and distribution capabilities. The analysis took into account the probabilities of oil supply disruptions, the availability of other sources of supply to offset the disruption, the elasticities of oil demand, and other market parameters. If we assume a one-billion barrel reserve and disruption lengths of six months or longer, then expanding the sustained drawdown and distribution capability beyond 5.5 million barrels per day is unwarranted, simply because the reserve would be exhausted in six months at that rate. Conclusions regarding the value of drawdown rate expansion thus depend strongly on assumptions regarding the expected length of disruptions, and on the likelihood of multiple, large disruptions in succession.

If assumptions are changed to allow for uncertainty in the duration of disruptions, and the rate of SPR drawdown is set optimally to hedge against possible future disruptions, then at least 14 of the 24 scenarios examined would appear to support expansion to a sustained capability of 7 million barrels per day. More efficient use of the SPR during disruptions would decrease the need to expand its drawdown and distribution capability compared to a policy of drawing down oil to offset as completely as possible any shortfall in oil supply.

In a series of short experiments by Leiby,² the DOE SPR planning model DISSPR was simulated to generate statistics on the frequency and magnitudes of expected drawdowns. These results contributed to the study of SPR drawdown enhancement. They also highlighted some limitations of the DISSPR model in cases where disruptions are somewhat less rare than was assumed in the January 1990 Interagency SPR study. Given the structure of the DISSPR model, the time required for SPR refill and the value of hedging against future disruptions is not fully accounted. Consequently, DISSPR results are more supportive

of higher drawdown rates, and DISSPR associates less value with sheer size/capacity expansion.

In a related effort, the method of response surface modeling is being applied to the larger SPR planning/optimization models, DISSPR and ORNLTEIS. The goal is to summarize their behavior and provide a spreadsheet-based planning tools for SPR planners.

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1. Trumble, David A. and Russell Lee 1991. "Benefits of Alternative Drawdown and Distribution Capabilities for the Strategic Petroleum Reserve: Results Under Revised Base Case Scenarios," Draft, October 31.
2. Leiby, Paul N. 1992. "DISSPR Drawdown Statistics and Incremental Benefits of Drawdown Enhancement," January 8.

7. EVALUATIONS AND ASSESSMENTS

R. R. Judkins

7.1 THE EXTERNAL COSTS OF FUEL CYCLES PROJECT

R. M. Lee

INTRODUCTION

This study is part of the U.S. Department of Energy's continuing National Energy Strategy. The purpose of this project is to analyze eight fuel cycles and four conservation options and to provide estimates of their impacts on environmental resources and on human health and safety. These impacts are estimated in terms of social costs and benefits. The assessments are being done in collaboration with a research team under the Commission of the European Communities (CEC). Oak Ridge National Laboratory and Resources for the Future are the principal research institutions for the U.S. team.

DISCUSSION OF CURRENT ACTIVITIES

Technical meetings with the CEC team were held in Oxford, UK, on October 24-25 and in Paris on October 28-29. The Oxford meetings covered an extensive review of the work on the coal fuel cycle and recent CEC papers documenting their work to date. The Paris meetings concentrated on the matrices and priorities for the uranium fuel cycle to be led by the CEC team.

A white paper was written during October on "Historical Responses to Address Externalities." In November, a number of interim documents were written by team members to contribute to the report for the coal fuel cycle. A synthesis report was done on the emissions data for the coal fuel cycle. Two documents were submitted on the air modeling tasks for the transport of power plant emissions, a report was drafted on the ecological impacts, and a draft paper was submitted on marginal damages versus externalities.

In December, a draft document "The External Costs of Fuel Cycles: Background Document to the Approach and Issues" was prepared. This report provides an overview of the U.S. study and the methodological choices that were made to conduct the research. The

report also includes a review of ecological and health impacts (using the coal fuel cycle as a reference case), and methods for valuing impacts and deriving damages.

In February and March, two reports on the oil fuel cycle were completed. The first discusses fuel stages, activities, and pollution; the second presents emissions from major oil fuel cycle activities.

A preliminary draft was completed for the coal fuel cycle externalities report. The report summarizes the assessment of existing literature to estimate damages and benefits from the coal fuel cycle. It discusses the regional reference environments, the benchmark technology, and priority impacts, and provides an impact and damage analysis. The study approach is framed by economic considerations of decision making to select fuel cycle options. The perspective is strictly forward looking: the study emphasizes the incentives faced by current and future decision makers and the ramifications for economic welfare. Economic valuation is used to monetize physical impacts. The Damage Function Approach is used to frame the incremental damages problem: it attempts to combine natural science and economics to reveal as many changed relationships from the incremental investment as possible (see Figure 1). Updates were performed for several sections of the report and internal reviews were begun.

Draft sections of reports on the other fuel cycles are underway.

**Figure 1. Impact-Pathway
Damage-Function Approach**

8.0 COAL STRUCTURE AND CHEMISTRY

N. C. Cole

8.1 INVESTIGATION OF COAL SURFACES AND INTERFACES

V. J. Tennery

INTRODUCTION

Diffuse reflectance infrared spectroscopy (DRIS) was used as a major instrumental technique for studying the spectral regions in all of the coals of the Argonne Premium Coal Sample (APCS) set to obtain information regarding the stretching and bending frequencies of the various bond types found in the coals represented by this highly standardized set of coal specimens. This technique clearly delineates the O-H stretching frequencies from about 3500 to 2500 wave numbers. It was also a good tool for studying the complex frequency regime from about 2000 to 500 wave numbers, representing a dense regime of bending modes. Fourier self deconvolution was used to distinguish details in the "hydrocarbon" spectral region around 3000 wave numbers. Pocahontas No. 3 coal was found to have a minimum of seven spectral peaks in this region. The "coalification" of the various materials in the APCS was clearly discernible from the details observed in the region near 3000 wave numbers. For example, Beulah Zap, a lignite, and Wyodak, a sub-bituminous, both presented relatively simple and weak spectral responses in the O-H stretching frequency range, whereas Upper Freeport, a medium volatiles bituminous, and Pocahontas No. 3, low volatile bituminous, both exhibited rich spectral detail in this region.

Studies of coal samples were carried out to determine the initial effects of oxidation upon the coal structures. These oxidations were often carried out at 300°C for periods up to 200 h. Large changes were observed in the spectra near 3000 wave numbers, indicating the oxidation of the coal surface from these exposures.

Additional work was done in studying the surface area and porosity in a number of these coals.

Transmission electron microscopy (TEM) techniques were developed for characterizing the interfaces between included minerals and the coal structure in a number of the coals, but most of the effort was focused on Pittsburgh No. 8, a high volatile bituminous which was considered representative of many bituminous coals. Observations of pyrite microcrystals with framboid structures in bulk coal specimens revealed the surprising result that a significant fraction of individual crystallites were in fact polycrystalline rather than single crystal. Further studies of macro single crystals of pyrite also revealed that all "single crystals" studied actually consisted of a system of small microcrystals even though the object appeared as a pyrite single crystal. Oxidation of the pyrite resulted in the formation of a surface film of goethite that coats the pyrite. Pyrrhotite was also observed on large crystals.

The research for coal surfaces and interfaces has been completed. The report was prepared as an ORNL/TM report.

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