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**Advanced Research and  
Technology Development (AR&TD)  
Materials Program Implementation Plan  
for  
Fiscal Years 1990 Through 1994**

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U.S. DEPARTMENT OF ENERGY  
OFFICE OF FOSSIL ENERGY

ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT (AR&TD)  
MATERIALS PROGRAM IMPLEMENTATION PLAN  
FOR FISCAL YEARS 1990 THROUGH 1994

Compilers

R. R. Judkins and D. N. Braski

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Date Published: March 1990

Research sponsored by the U.S. Department of Energy,  
Advanced Research and Technology Development  
Materials Program  
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Prepared by the  
FOSSIL ENERGY MATERIALS PROGRAM OFFICE  
OAK RIDGE NATIONAL LABORATORY  
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- ORNL/TM-7612      *Advanced Research and Technology Development Fossil Energy Materials Program Plan for FY 1981*, R. A. Bradley and R. R. Judkins, July 1981
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- ORNL/TM-8954      *Advanced Research and Technology Development Fossil Energy Materials Program Implementation Plan for Fiscal Years 1984 Through 1988*, R. A. Bradley and P. T. Carlson, October 1984
- ORNL/TM-9328      *Advanced Research and Technology Development Fossil Energy Materials Program Implementation Plan for Fiscal Years 1985 Through 1989*, R. A. Bradley and P. T. Carlson, February 1985
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- ORNL/TM-10242     *Advanced Research and Technology Development Fossil Energy Materials Program Implementation Plan for Fiscal Years 1987 Through 1991*, R. R. Judkins and P. T. Carlson, September 1987

## FOREWORD AND ACKNOWLEDGMENTS

This document was prepared by the staff of the Fossil Energy Materials Program, Metals and Ceramics Division, Oak Ridge National Laboratory. Guidance for the preparation of this plan was provided by E. E. Hoffman, Department of Energy Oak Ridge Operations, and by D. J. Beecy and J. P. Carr, Department of Energy Fossil Energy Office of Technical Coordination.



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ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT MATERIALS PROGRAM  
IMPLEMENTATION PLAN FOR FISCAL YEARS 1990 THROUGH 1994\*

Compiled by  
R. R. Judkins and D. N. Braski

ABSTRACT

This program implementation plan for the Department of Energy Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program reviews the technical issues and the materials research and development needs of fossil energy technologies. The status and plans for research and development activities in the AR&TD Materials Program to meet those needs are presented. Detailed information about these plans is provided for FY 1990 through FY 1991, and long-range plans are described for FY 1993 and FY 1994.

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\*Research sponsored by the U.S. Department of Energy, Fossil Energy AR&TD Materials Program [DOE/FE AA 15 10 10 0, Work Breakdown Structure Element ORNL-4(A)] under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.



PART I  
INTRODUCTION



## 1. INTRODUCTION

### 1.1 PROGRAM DESCRIPTION AND OBJECTIVES

This implementation plan for the Department of Energy Office of Fossil Energy Advanced Research and Technology Development (AR&TD) Materials Program was prepared in cooperation with the U.S. Department of Energy (DOE) Oak Ridge Operations (ORO) Office and the DOE Fossil Energy Office of Technical Coordination.<sup>1</sup> It describes the program objectives, organization, and responsibilities of the various participants on the program, and is consistent with the Multi-Year Summary Program Plan issued by the Fossil Energy Office of Technical Coordination.<sup>1</sup> In particular, details of planned activities for FY 1990, FY 1991, and FY 1992 and an indication of anticipated activities through FY 1994 are presented. This implementation plan is for a comprehensive materials program, and the funding indicated is an estimate of the funds required for the comprehensive program. Of course, the actual funds that are available in any fiscal year will depend on congressional appropriations, and the technical program will be adjusted for consistency with those appropriations. We have also included descriptions of new and expanded initiatives in this plan. These new and expanded initiatives are particularly important or promising developments; they include the development of catalyst supports for coal liquefaction, solid electrolyte (including fuel cells) materials, iron aluminides, ceramic filters, ceramic membranes, advanced materials processing (ceramics and metal alloys), technology transfer, and coatings and claddings.

The goals of the AR&TD Materials Program are to develop a fundamental understanding of materials and their performance in fossil energy systems and, based on this understanding, develop materials that will perform satisfactorily in the hostile environments of fossil energy plants. Exploratory research of new materials which have the potential to improve the performance of existing fossil systems or enable the development of new fossil systems will also be conducted.

The scope of the program encompasses all fossil energy systems, and we attempt to address the materials needs of these systems with a program that is generic and crosscutting, i.e., not specific to a single fossil energy technology.<sup>2</sup>

There is a range of research and development activities within the DOE Fossil Energy Program. Within this spectrum, the AR&TD Materials Program lies between the basic research of DOE Energy Research and the process and engineering development of the Fossil Energy Technology R&D programs. The AR&TD Materials Program is concerned with fundamental and exploratory research. The Program is oriented toward novel and highly innovative concepts, and it develops ideas, understanding, and knowledge that is broadly relevant to fossil energy technologies. Because of the nature of the research, it is high risk but with potential high payoffs occurring in the short-, mid-, and long-term time frames.

The fundamental and exploratory research activities provide a very strong base for further advances on the process and engineering development activities of the Technology R&D programs. The coupling of the AR&TD Materials Program with the Technology R&D programs may produce results with broad applications across numerous technologies, thus the terms generic and crosscutting. Tables 1.1.A, 1.1.B, 1.1.C, and 1.1.D provide an indication of the broad applicability of the AR&TD Materials Program. In this table, ongoing and planned research is correlated with the fossil energy technologies.

Notwithstanding this generic and crosscutting approach, we attempt to develop lower-cost materials where cost is a major factor in limiting the use of an advanced coal system.<sup>3</sup> In addition, performance criteria are established for the materials in specific fossil energy systems. For example, our iron aluminide development is based primarily on performance criteria of heat exchange devices in coal gasification plants, but these alloys are expected to also have widespread use in other fossil energy applications and in various industrial and automotive (e.g., exhaust) applications. This approach helps to assure a larger commercial market and, by so doing, assures

Table 1.1.A Relationships among materials research program elements and technology areas of the Advanced Research and Technology Development (AR&TD) Materials Program

Program Element	Technology areas					
	Coal preparation	Coal liquefaction	Coal gasification	Heat engines and heat recovery	Combustion systems	Fuel cells
Ceramics						
ORNL-1(A)	X	X	X	X	X	X
ORNL-1(C)	X	X	X	X	X	X
GT-1	X	X	X	X	X	X
GT-1(A)	X	X	X	X	X	X
LANL-1	X	X	X	X	X	X
INEL-1(A)	X	X	X	X	X	X
INEL-1(B)	X	X	X	X	X	X
VPI-1	X	X	X	X	X	X
NCAT-1	X	X	X	X	X	X
NIST-1	X	X	X	X	X	X
ANL-1	X	X	X	X	X	X
ORNL-1(D)	X	X	X	X	X	X
PNL-1	X	X	X			X
SNL-1		X	X			X
ORGDP-1	X	X	X	X	X	X
ORNL-1(B)	X	X	X	X	X	X
INEL-1(C)	X	X	X	X	X	X

Table 1.1.B Relationships among materials research program elements and technology areas of the Advanced Research and Technology Development (AR&TD) Materials Program

Program element	Technology areas					
	Coal preparation	Coal liquefaction	Coal gasification	Heat engines and heat recovery	Combustion systems	Fuel cells
New alloys						
ORNL-2(B)		X	X	X	X	
CU-2		X	X	X	X	
USC-2		X	X	X	X	
B&W-2		X	X	X	X	
UTN-2		X	X	X	X	
FW-2		X	X	X	X	
SC(1.U)-2		X	X	X	X	
ORNL-2(A)	X	X	X	X	X	
ORNL-2(F)	X	X	X	X	X	
INEL-2	X	X	X	X	X	
CSM-2	X	X	X	X	X	
HWRL-2	X	X	X	X	X	
SC(1)-2(A)		X	X	X	X	
OSU-2	X	X	X	X	X	X
WHC-2	X	X	X	X	X	X
SC(1)-2(C)	X	X	X	X	X	X
SC(1)-2(D)	X	X	X	X	X	X

Table 1.1.C Relationships among materials research program elements and technology areas of the Advanced Research and Technology Development (AR&TD) Materials Program

Program element	Technology areas					
	Coal preparation	Coal liquefaction	Coal gasification	Heat engines and heat recovery	Combustion systems	Fuel cells
Corrosion and erosion research						
ANL-3	X	X	X	X	X	X
BCL-3	X	X	X	X	X	X
CWR-3	X	X	X	X	X	X
UES-3	X	X	X	X	X	X
UTN-3	X	X	X	X	X	X
UCIN-3(A)	X	X	X	X	X	X
LBL-3	X	X	X	X	X	X
ORNL-3(B)	X	X	X	X	X	X
UCB-3	X	X	X	X	X	X
UND-3	X	X	X	X	X	X
ORAU-3	X	X	X	X	X	X
SC(I)-3	X	X	X	X	X	X
UCIN-3	X	X	X	X	X	X
NIST-3	X	X	X	X	X	X
MIT-3	X	X	X	X	X	X

Table 1.1.D Relationships among materials research program elements and technology areas of the Advanced Research and Technology Development (AR&TD) Materials Program

Program element	Technology areas					
	Coal preparation	Coal liquefaction	Coal gasification	Heat engines and heat recovery	Combustion systems	Fuel cells
Technology development and transfer						
BCL-4	X	X	X	X	X	X
NIST-4	X	X	X	X	X	X
ORNL-4(B)		X	X		X	
SOR-4		X				
3M-4	X	X	X	X	X	X
TCRD-4			X	X	X	
SC(I)-4(A)	X	X	X	X	X	X
SC(I)-4(B)	X	X	X	X	X	X
SC(I)-4(C)				X	X	
SC(I)-4(D)	X	X	X	X	X	X
SC(I)-4(E)	X	X	X	X	X	X
SC(I)-4(F)	X	X	X	X	X	
SC(I)-4(G)		X	X	X	X	
SC(I)-4(H)	X	X	X	X	X	X

greater industrial interest in transferring the important technological developments of the program. The development of highly advanced materials that will allow the extension of fossil systems to higher performance levels will also be promoted. There is indeed a synergism between the fundamental and exploratory research of the AR&TD Materials Program and the Technology R&D programs. The promising concepts and knowledge established by the fundamental and exploratory research can be extended and advanced to process and engineering development programs, and the results of large-scale testing often identify needs for new fundamental and exploratory research.

Work on the program is identified by materials disciplines, or program elements, including ceramics, new alloys, corrosion and erosion research, and technology assessments and transfer. The ceramics research includes activities on structural ceramic composites, solid state electrolyte systems, catalyst support materials, ceramic membranes, ceramic filters, and new materials processing techniques. Research and development of new alloys includes work on advanced austenitic steels and iron aluminides. The corrosion and erosion research includes fundamental studies of corrosion and erosion processes. The fourth element addresses technology development and transfer. The organization of these activities is shown in Fig. 1.1. Those readers familiar with the program will notice some differences in this organization from that of prior years. Historically, the AR&TD Materials Program has focused on the development of structural materials, i.e., materials of construction, for fossil energy plants. This new organization recognizes the value and need of materials science in the development of process materials. For example, the work on catalyst supports for coal liquefaction is directed toward understanding the structure-properties relationships of ceramic catalyst supports. By understanding these relationships, we hope to produce catalyst supports with suitable properties for a variety of coal conversion systems.

Implementation of the AR&TD Materials Program has been decentralized to DOE-ORO, with ORNL as the technical support contractor. A

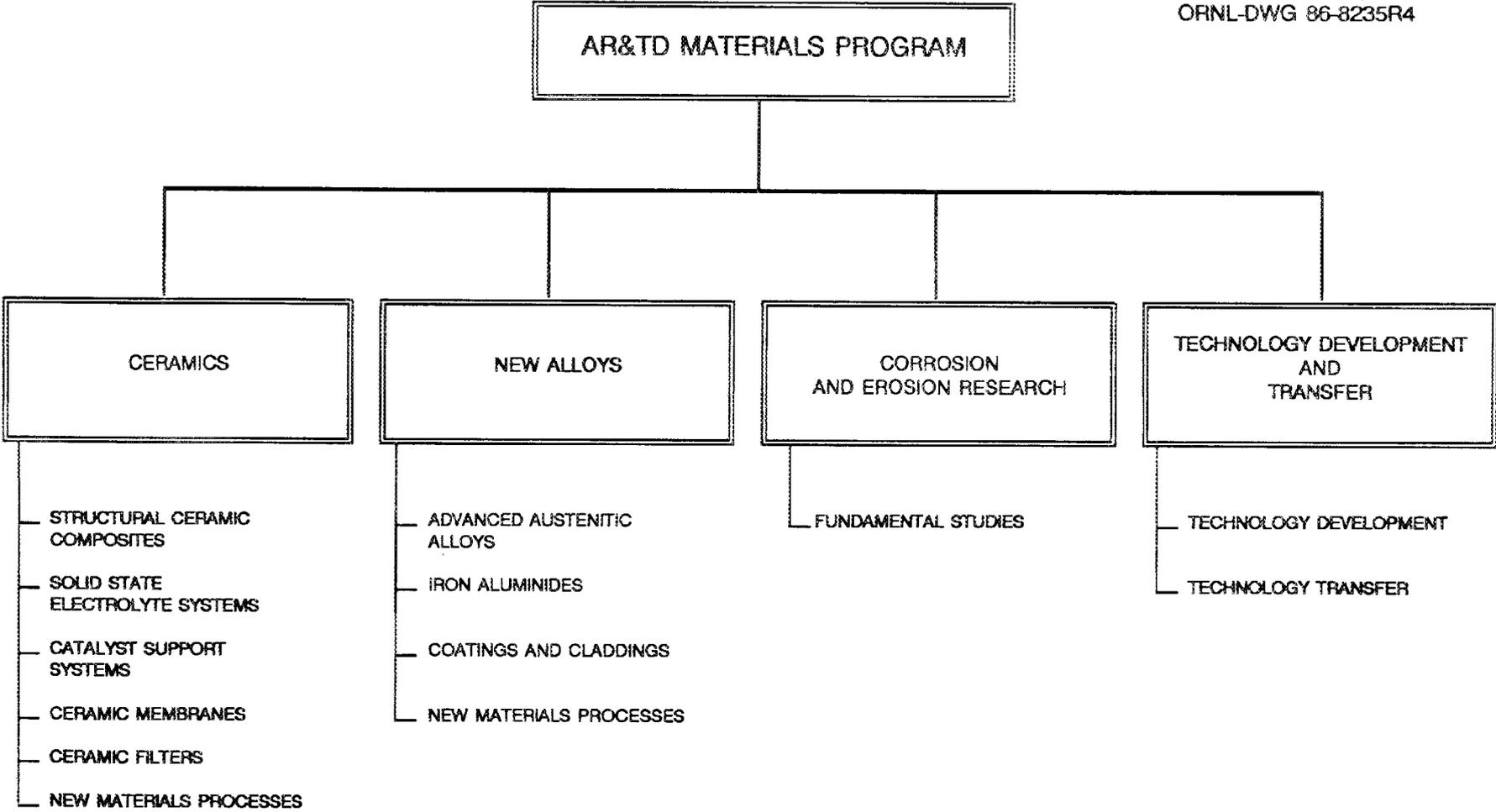


Fig. 1.1. Organization of research activities on the AR&TD Materials Program.

broad base of participation exists on the program and includes national and government laboratories, universities, and industrial research centers. All work on the program is technically monitored by materials experts. Though independent, these organizations are all focused on the particular goals of the program and, in many instances, the research is complementary. This complementary approach works well, and it provides a range of talents for various aspects of a materials development effort. As an example of this approach, the work on advanced austenitic alloys is being conducted at Oak Ridge National Laboratory (alloy development), Cornell University (property evaluations), Babcock and Wilcox Company (fabricability studies), the University of Tennessee (welding and joining), and Foster Wheeler Development Corporation (corrosion studies). This concerted effort has resulted in alloys with outstanding properties for a variety of applications.

In this Plan, relevant research and development needs of the various fossil energy technologies are identified and discussed in Part II. Identified R&D needs are generally those that are appropriately addressed on the AR&TD Materials Program. The individual chapters of Part II are not meant to be exhaustive in identification of materials research needs. Many short-range materials problems are being appropriately addressed by the Technology R&D programs.

Descriptions of ongoing and planned activities are presented in Part III. Tables in each chapter of Part III, Current and Planned Projects in the AR&TD Materials Program, present funding levels for each project. The funding distribution for FY 1990 is current; for subsequent years, the distribution reflects our assessment of needs. These needs have been identified by general in-house assessments,<sup>4-5</sup> conducted by subcontractors,<sup>6-7</sup> by research and development proposals, by discussions with individuals and organizations interested in fossil energy materials development, and from a series of technology base reviews conducted annually by the DOE Fossil Energy Office of Technical Coordination.<sup>8</sup> In addition, the AR&TD Materials Program interacts with other DOE research programs, such as the Materials Sciences Program of the Office of Basic Energy Sciences (BES), and through participation in the activities of the Energy Materials Coordinating Committee (EMaCC).<sup>9</sup>

Numerous other interactions occur between the AR&TD Materials Program and other DOE programs to ensure that the goals of the program are consistent with the needs of developing fossil energy technologies. To maintain an awareness of current research needs, the program management staff and principal investigators in the AR&TD Materials Program routinely receive news bulletins from various programs and organizations (the Electric Power Research Institute, the Gas Research Institute, etc.) on subjects such as welding, erosion, structural ceramics, alloy development, and other areas of mutual interest. We intend to revise this program implementation plan annually, and we welcome suggestions for these future revisions.

As a final note, our goal is to have the very best program possible. The goal of an optimum plan requires good planning, and good research. Our budget is limited, and to perform all the research needed, an increase in the budget would be required. As a result of these budget limitations, funding of projects by the Program is highly competitive. We are continually seeking new projects and welcome suggestions for new projects for the Program. Generally, brief concept papers that provide sufficient information to permit a determination of interest are preferred to unsolicited proposals. Selection of projects on the Program is generally by competitive procurement. Virtually all of our research projects at industrial research centers have been selected by a competitive process. We anticipate that our selection of future university projects will also emphasize competitive procurement.

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PART II

MATERIALS RESEARCH AND DEVELOPMENT NEEDS  
OF FOSSIL ENERGY TECHNOLOGIES



## 1. INTRODUCTION

Part II covers a spectrum of fossil energy technologies and the technical issues relating to materials of construction. Other technical issues related to coal liquefaction, coal gasification, structural ceramics for heat engines and heat recovery, combustion systems, fuel cells, coal preparation, technology assessment, and technology transfer are discussed.



## 2. COAL LIQUEFACTION

### 2.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

In direct liquefaction processes, coal is reacted with high-pressure gaseous hydrogen and/or hydrogen in a donor oil solvent. The materials issues that are addressed in the program are those involving the direct reaction of coal and hydrogen in a liquid slurry. Several processes have been demonstrated in the Wilsonville, Alabama, pilot plant that has been in operation since 1974. For this discussion, the direct liquefaction processes are divided into the major process areas: coal and slurry preparation, preheaters, dissolver vessels, gas separation vessels, heat exchangers, solids separation, product-solvent separation, pumps, and transfer lines.<sup>1</sup>

The research and development program (for coal liquefaction materials) described in Part III is based almost entirely on the needs of direct coal liquefaction plants. However, there are materials needs for advanced processes which are currently at a bench-scale of development for which many of the current and planned activities in the AR&TD Materials Program are appropriate. These include the areas of erosion, corrosion, and erosion-corrosion.

#### 2.1.1 Coal and Slurry Preparation System

The materials requirements for the coal and slurry preparation system of coal liquefaction plants are fairly well established. Wear, erosion, and corrosion have been the main problems in the various components. For the size-reduction equipment, carbon steel is the currently accepted material. The abrasion and wear of these components is substantial, especially with high-mineral-content coals, but the materials problems in this area do not significantly restrict commercialization.

#### 2.1.2 Preheaters

Coal liquefaction plant preheaters are generally helically coiled pipes heated by oil or gas burners. The preheaters receive a three-phase stream containing coal, solvent, and hydrogen-rich gas from the slurry feed pump. The temperature of this preheater feed is in the

range 38 to 260°C and the pressure is in the range 14 to 21 MPa. The slurry leaves the preheater at a temperature between 400 and 450°C and at a pressure somewhat lower than the inlet pressure. Considerations in the selection of the preheater material include erosion, hydrogen and hydrogen sulfide attack, and chloride stress-corrosion cracking, all of which could result from contact with the slurry. The outside of the preheater is exposed to combustion gases.

### 2.1.3 Dissolver Vessels

Dissolvers for direct coal liquefaction plants are pressure vessels containing coal slurried in process oils at temperatures ranging from -400 to -460°C in a reducing atmosphere consisting primarily of hydrogen with gaseous hydrocarbons and impurities, particularly H<sub>2</sub>S, formed by reactions with impurities in the coal. Total pressures in the dissolvers range from ~14 to ~21 MPa. Vessel sizes vary but may be about 4 m in diameter and 15 to 18 m tall, with a wall thickness of 0.3 to 0.4 m. Considerations that must be addressed in the design of these systems include pressure, temperature, fabrication and welding procedures, steel composition, temperature cycling, and partial pressures of hydrogen and hydrogen sulfide.

At the temperatures and pressures experienced by these vessels, low-alloy steels may experience hydrogen attack, which occurs when hydrogen reacts with carbon in solution in the steels to form methane. This internal decarburization weakens the steel. Temper and creep embrittlement of low-alloy steels is also of concern in the selection of materials for these vessels. Materials selection for high-temperature hydrogen service is based on Nelson curves, which are derived from experience and indicate the limits of temperature and pressure below which specific alloys have not failed in service.<sup>2</sup>

The conventional practice for joining sections of thick-walled vessels, including nozzles, is submerged arc welding (SAW). Other welding processes that offer some advantages when used alone or in combination with SAW include narrow-groove variants of gas metal arc welding (GMAW) and hot-wire gas tungsten arc welding (HW-GTAW), electron beam welding, and electroslag welding. Adaptation of SAW to vertical and horizontal welds and improvement and automation of the

shielded metal arc welding process may also be useful in fabrication of these vessels.

#### 2.1.4 Gas Separation Vessels

The gas separation vessels downstream from the dissolver present similar, although less severe, problems to those of the dissolver, namely, the containment of a high-pressure and high-temperature slurry in an atmosphere consisting principally of hydrogen with gases such as hydrogen sulfide.

Materials selection criteria for the gas separation (flash) vessels are similar to those of the dissolver vessels. The intermediate- and low-pressure flash vessels also require a weld overlay of type 347 stainless steel for corrosion protection.

Fabrication techniques for the gas separation vessels are the same as those for the dissolver vessels but are somewhat simpler because of the smaller overall dimensions and wall thicknesses.

#### 2.1.5 Heat Exchangers

Coal liquefaction plants, like petroleum refineries and chemical processing plants, require a large number of heat exchangers for adding and recycling process heat. Demonstration and commercial-size plants, because of the demands of economics and process thermal efficiency, will have numerous heat exchangers handling many different process streams. Many of these streams do not pose special problems, so materials selection and design can be based on refinery and chemical plant experience. Unique to direct liquefaction are several problem areas related to the presence of solids in the process streams and to the high operating temperatures and pressures.

In the pilot plants, the first heat exchanger contacted by the process stream is the reactor effluent cooler, which handles the solid, liquid, and gas mixture that leaves the reactor at temperatures as high as 460°C and pressures up to 21 MPa. Both air- and water-cooled exchangers have been used for this application, but not without some difficulties due partly to the large thermal gradients. In the current designs for demonstration and commercial plants, the reactor effluent is fed directly to a separator vessel, thus eliminating the need for a

heat exchanger to be operated under these especially severe conditions. Instead, a heat exchanger is used to cool the overhead product from the first separator vessel, which is essentially free of solids but rich in  $H_2S$  and other corrosive gases. Consequently, the exchanger tubes will probably be fabricated from an austenitic stainless steel. In the demonstration plant designs (and for most of the pilot plants), a series of separator vessels operating at progressively lower temperatures further separate the inorganic gases and liquids and the organic products. Before each of these separator vessels, a heat exchanger is used to condense a portion of the vessel feed. These exchangers are generally tube-and-shell type and, for all but the lower-temperature applications, the tubes are of austenitic stainless steel (or duplex alloys where  $NH_4Cl$  and water are condensed) and the shells are of carbon steel. For the lowest temperatures, the tubes and shells are generally carbon steel.

#### 2.1.6 Solids Separation

One of the major differences between liquefaction of coal and refining of petroleum is the need to handle and remove the residue (ash and unreacted coal) remaining after hydrogenation of coal. Removal of this residue has been attempted by using filters, centrifuges, hydroclones, vacuum distillation, and proprietary solvent de-ashing techniques. In some of the operating pilot plants, vacuum distillation was used along with one of the other techniques.

Besides the mechanical problems, corrosion and erosion have occurred on the solids separation devices. Erosion has been noted in vacuum distillation vessels at the point where the incoming slurry impacts the vessel wall. It has also been observed in reflux and recirculation lines around these vacuum vessels. Thinning of filter screens has been reported and is probably due to an erosion-corrosion phenomenon. In the portions of the vessels operated at temperatures  $>230^\circ C$ , appreciable corrosion of low-alloy steels has been noted. This corrosion, which involves sulfidation of the steel, has been alleviated by use of austenitic stainless steels.

Knowledge of materials performance in vessels of solvent de-ashing units is limited because of the limited operating time accumulated and

the restrictions imposed on release of proprietary information about these units. It is known that some operations are performed at temperatures well above 260°C, and sulfidation could be a problem if alloy steels are not used.

#### 2.1.7 Product-Solvent Separation

Liquid products are separated in coal liquefaction plants in fractionation columns operated at or slightly above atmospheric pressure. In some processes, the feed to the columns contains appreciable solids, while in other cases the feed streams have been through a vacuum distillation and/or solids removal process. Some plants use a two-stage distillation in which a light oil or naphtha product (boiling point <175°C) along with residual water is removed in the first column. The temperature in the first column, the light oil fractionation column, generally ranges from ~285°C in the bottom to ~165°C at the top.

In most cases these are packed rather than trayed towers and no severe corrosion problems have been encountered, although corrosion of carbon steel has been reported in the higher-temperature portions of some of these towers. The second column, the higher-temperature fractionation column, operates with the bottom of the column at least 300°C and the top at least 200°C. Severe corrosion has been encountered in this type column in the 200 to 260°C range, and the extent of corrosion is proportional to the chlorine content of the feed coal. For processes in which a single fractionation column is used, the temperature range of that column is greater and sidestream withdrawals are generally used to remove some of the products. Severe corrosion in the 200 to 260°C range has also resulted when only one column has been used.

Thus, regardless of the number of columns used and the mode of operation and product withdrawal, corrosion has been confined primarily to the temperature range 200 to 260°C. Often little or no corrosion occurs in the column above or below the region in this temperature range.

Considerable study has been devoted to the mechanism and prevention of this corrosion. Amine hydrochlorides are transported to the fractionation columns, where they thermally dissociate above 240°C. The volatile dissociation products move up the columns until a temperature is reached at which appreciable recombination occurs. The higher boiling point of the compound leads to condensation and refluxing of the amine hydrochlorides. Thus, a trapping and concentrating mechanism exists within the column. On dissociation, the amine hydrochlorides dissolve in the process liquids to form acidic solutions, which react with (i.e., corrode) the containment materials. This corrosion may be controlled by alloy selection or by process modifications.

#### 2.1.8 Pumps

A significant number of pumps is required in a coal liquefaction plant to transfer a wide variety of fluids and slurries. Most requirements to handle separated organic liquids and sour water can be met by available centrifugal pumps with the materials choices based on petroleum industry experience. Care must be taken in the choice of seal designs and materials, because of the susceptibility of the more common elastomers to rapid degradation by coal-derived liquids. Frequently, seals employing fluorinated hydrocarbons with graphite, glass, and asbestos fibers are needed in such applications.

The most severe demands on pump design and materials selection are encountered in the handling of coal and ash slurries at elevated temperature.<sup>3</sup> The slurry pumping requirements can be roughly divided into four areas: coal feed preparation, reactor feed, slurry recirculation, and mineral-ash residue slurry transport.

In the coal feed preparation area, coal and process solvent, with or without recycled slurry, are blended. The slurry temperature is up to 230°C; the pressure is nearly atmospheric; and the solids content is up to 45%. Typically, centrifugal pumps are used in these low-head applications to circulate the feed slurry and deliver it to the reactor feed pumps. Erosion and erosion-corrosion are the principal materials concerns for pump internals.

In the reactor feed area, the pump requirements are more severe because coal slurry at temperatures up to 230°C must be pumped to

pressures as high as 24 MPa. Because of the high-head requirements, reciprocating pumps have been used almost exclusively, although experimental centrifugal pumps and alternative reciprocating pumps, such as the surge leg design, have been tested. In the reciprocating pumps the materials problems are associated with the plungers, check valves and seals. The solids in the slurry severely abrade all moving parts and the high temperatures can affect the packing and interfere with alignment. High-strength steel is required for the cylinders. Hard-facings and coatings, particularly on the plungers, have not yet provided adequate service life. Gearbox thermal insulation, cooling of pump parts, and the use of process solvent purge liquids reduce the frequency of maintenance. Tungsten carbide balls and Stellite seats have provided the best check valve performance.

For both recycle slurry and mineral-ash residue slurry transport, centrifugal and reciprocating pumps have been used, according to the head requirements. Materials choices and problems are similar to those for the other applications, although the higher temperatures (up to 400°C) usually require the use of higher-alloyed steel, such as the molybdenum-containing austenitic stainless steels, to prevent corrosion of the housings.

#### 2.1.9 Transfer Lines

Piping used to transfer coal-derived products from one vessel to another is exposed to environments that may cause erosion, sulfidation, hydrogen attack, and chloride and polythionic acid stress-corrosion cracking. Service temperatures range from ambient to 480°C, and pressures range from near atmospheric to 21 MPa. Materials used in the pilot plants have ranged from carbon steel through ferritic and martensitic stainless steels to austenitic stainless steels. The most serious pilot plant piping failures observed have been in so-called "dead legs," pipes in which there is normally no flow. They are used for mounting temperature- or pressure-sensing devices, safety relief valves, or vent lines. The common feature of these dead legs is that they usually operate at somewhat lower temperature than connecting piping, thus providing a site where water can condense.

### 2.1.10 Ceramic Catalyst Supports

Improvements in catalyst performance in coal liquefaction systems could provide higher throughput, lower temperature processing, and improved yield of high value liquids from coal. Although the technology exists to convert coal to liquid fuels, it is too expensive to allow for the establishment of a competitive synfuel industry. Development of advanced catalysts is a principal way to lower the costs of converting coal to liquids. Modest increases in catalytic activity and selectivity can have a major impact on processing costs and the market value of liquids produced.

Hydrous metal oxide (HMO) supported catalysts have great potential for conversion of coal and related materials to liquid fuels. Work sponsored by the DOE Pittsburgh Energy Technology Center's Exploratory Catalysis Program (Advanced Research-Coal Liquefaction) has shown that HMO-supported catalysts have similar reactivity at one-tenth the active metal loading of a commercial catalyst for coal liquefaction reactions. The AR&TD Materials Program has supported work on ceramic catalyst supports to use materials science techniques to explore the chemical and microstructural properties of HMO supported catalysts.

Additional work is needed to determine how synthesis conditions control the molecular and extended structure of HMO supports and how the support structure influences the reactivity and selectivity of catalysts used for coal conversion.

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### 3. COAL GASIFICATION

#### 3.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

Coal gasification processes have been summarized<sup>1</sup> and can be classified into several major types: (1) fixed bed, (2) fluidized bed, (3) entrained flow, and (4) molten bath.

In a fixed-bed gasifier, sized coal is fed into the top of the gasifier. It moves slowly downward in a bed fixed on a grate, through which steam and air or oxygen pass upward. At the bottom of the bed, carbon reacts with oxygen to form carbon dioxide in a narrow oxidation zone, above which the endothermic reactions of carbon with steam and carbon dioxide initiate the formation of carbon monoxide and hydrogen. At the top of the bed the coal undergoes successive drying, devolatilization and reaction with oxygen and steam, and the volatiles crack to form hydrogen, methane and light hydrocarbons.

In fluidized-bed gasifiers, the maximum particle size is much smaller than in fixed-bed operation and the gas is passed up through the bed with a velocity high enough to fluidize the particles. The temperature of the exit gas is approximately equal to that of the bed. Fluidized-bed gasifiers can use a wide range of coals, but pretreatment or some other techniques may be necessary with caking coals that can agglomerate in the bed with loss of proper fluidization. The most common type of pretreatment is mild oxidation, usually with heated air.

In the entrained-flow process, pulverized coal is carried through the gasifier with the gas. A separator is required to remove the particulate residue from the product gas. Because the reaction rates tend to decrease as the particles pass through the reactor, high temperatures are required to achieve the necessary conversion with a reasonable reactor size. At these high temperatures, little or no tar and very little methane are produced. To improve the thermal efficiency of the process, the relatively high-temperature product gas is usually passed through a heat recovery system.

A molten bath can serve as an effective coal gasification medium, since some baths have good heat transfer and sulfur absorption properties. Materials studied or used as baths have included fused

salts and molten metal or coal slag. Such systems accept all types of coal and, within limits, are insensitive to particle size. A vertical partition may be used to produce separate sections of a common molten bath. The exothermic air-blast phase and the endothermic water gas phase may be applied to these separate sections. By this technique, synthesis gas relatively free of nitrogen may be produced.

The major materials problems with gasification processes generally are associated with (a) resisting the aggressive gases, (b) feeding solids, and (c) removing ash. The severity of materials problems in gasification processes varies greatly with processing parameters, especially the temperature, the pressure, and the composition of the coal. The sulfur-bearing compounds of the coal gas atmosphere, chiefly  $H_2S$ , are very injurious to metallic materials of construction, especially under the more reducing conditions (low oxygen-to-sulfur partial pressure ratio). The coal gas atmosphere may also contain sodium and/or potassium (<0.5%), and, if so, alkali attack on the refractory liners of gasifiers may be a problem.

Although the materials requirements for coal gasification processes vary considerably with the operating conditions of the process, the major materials considerations can be described under the following categories: coal preparation, coal feeding systems, gasifier shell and refractories, gasifier internals, gas quench and heat recovery, raw gas treatment, and piping and transfer lines.

### 3.1.1 Coal Preparation

With minor exceptions, the coal handling facilities in the front end of the gasification plant are constructed of carbon steel. The materials problems in this area are generally confined to wear and abrasion, and suitable construction materials have been largely established by prior experience in handling solids in the electrical utility and mining fields. These problems are addressed by using hard alloy chute liners and wear plates and the application of hardfacing materials where the wear is more severe.

### 3.1.2 Coal Feeding System

One of the critical components of coal gasification plants is the system for feeding coal into the gasifier. Currently, lock hopper systems with two ball valves in series are used for transferring dry solids (coal, char, and slag) into and out of the gasifier when the operating pressure is ~2 MPa. Typically, the ball of these valves is constructed of type 316 stainless steel coated with hard chromium plate, and the trim insert on which the ball seats is Stellite 6. Rubbing wear between the two sealing surfaces, aggravated by abrasive coal constituents, results in eventual loss of pressure and necessitates periodic overhauling of the valves.

For gasification processes operating at 3.5 MPa or higher, the coal feed is generally introduced into the pressure-temperature envelope as a water or oil slurry, using a high-head reciprocating plunger pump to attain the operating pressure. The packing seals of the plunger pumps, which are composed of graphitic or special organic fabrics, pick up abrasives from the slurry and generally have very limited lifetime. Parallel pumps with planned outages for replacing packings would be needed in commercial plants.

### 3.1.3 Gasifier Shell and Refractories

The principal candidate construction material for the gasifier vessel of commercial substitute natural gas plants is 2½ Cr-Mo steel. The plant typically would have two or more streams with 5- to 10-m-diam and 150- to 250-mm-thick gasifier vessels. Designs generally are of two basic types: (a) water-jacketed shell and (b) unjacketed shell. Because gasifier environments contain high concentrations of steam, dew points up to 215°C can be expected. Where the design temperature for the wall is below the dew point, the shell is exposed to an aqueous phase containing dissolved H<sub>2</sub>S, CO<sub>2</sub>, and NH<sub>3</sub> in equilibrium with the gasifier environment; depending on the pH, such solutions may be corrosive to medium- and low-alloy steels. For the unjacketed type, where the wall temperature is allowed to exceed ~260°C, dry sulfide scaling from the H<sub>2</sub>S component of the gas environment becomes a concern. The gasifier shell is generally lined with a base refractory plus a hard, high-density, gas-side refractory

chosen to resist the reactor environment. In applications where the combustion gas temperatures range from 1400 to 1750°C (slagging gasifiers), corrosion by the liquid slag is a prime consideration.

#### 3.1.4 Gasifier Internals

The most challenging materials problems in gasification processes relate to the essential metallic components that must function in the hottest regions inside the gasifier. Internal components include: contact thermometers, char and coal burners, tuyeres, bed stirrers, and grates. Where the operating temperature does not exceed 1000°C, the metal components are generally fabricated of iron-, nickel- and cobalt-base heat-resistant alloys that rely principally on chromia for corrosion resistance. A major impediment to the performance of these materials is high-temperature sulfidation. Although such materials have traditionally served in oxidizing atmospheres where adherent oxide films provide protection, coal gasification environments generally are only marginally oxidizing and may contain reactive ash and slag particles. The metals react with sulfur as well as oxygen, leading to eventual catastrophic breakaway corrosion by mechanisms that are not well understood. Additionally, entrained solids often contribute a synergistic erosive effect.

#### 3.1.5 Gas Quench and Heat Recovery

Coal gas is generally quenched to facilitate the gas-treating steps downstream and reduce corrosion-erosion of components. Both overhead water spraying units and heat exchanger systems are used. In water quench systems the usual metallic liner that contains the water spray is subject to severe cavitation and cracking.

#### 3.1.6 Gas Separation/Ceramic Membranes

The development of membranes with high selectivity and flux capabilities has led to the commercial-scale use of membranes to separate gaseous components from gas mixtures. For example, modular membrane separation systems are now commercially available for hydrogen purification and recovery in ammonia plants, manufacture of oxygen-enriched air, sweetening of sour natural gas, and recovery of carbon dioxide from well-head gas in enhanced oil recovery operations. However, the

membranes used in these systems are thin film composites of polymeric organic materials which have limited thermal stability and are susceptible to abrasion and chemical attack in harsh environments. Therefore, these membranes have not found applications in high-temperature separation processes. Ceramic membranes may withstand such hostile environments. Although the permeability of several gases in various inorganic materials has been studied, there has been no large-scale application of inorganic membrane separations of gases except for uranium enrichment. Gas permeabilities of metals such as tungsten, molybdenum, iron, copper, nickel, silver, and palladium, and alloys of these metals have been studied. Ceramics and porous metals have also been tested as supports for deposition of metal films of vanadium and aluminum, and for membrane coatings of zirconium oxide, nickel oxide, and titanium oxide. Recently, inorganic polymeric membranes such as poly-phosphazenes and organic-inorganic membranes containing heteropoly acids and salts have been prepared. Two potentially important industrial applications of inorganic membranes have been identified. These include recovery of hydrogen from synthesis gas at high temperature and in chemically harsh environments and for removal of acid gases from raw synthesis gas at 650 to 1000°C. Hydrogen is an important and valuable industrial raw material that has numerous uses in the chemical and fuels industries. Synthesis gas produced in coal gasification is primarily hydrogen and carbon monoxide. However, isolating the hydrogen from the other gases produced requires low-temperature operations such as pressure-swing adsorption (at 4 to 40°C) or cryogenic separation. Polymeric membranes have also been suggested to separate hydrogen for ammonia synthesis. However, because of membrane limitations, these operations are generally performed at relatively low temperatures on clean gas streams. If technology could be developed to separate the hydrogen from the raw gas at high temperatures, it would significantly lower the cost of hydrogen production. Ceramic membranes should be developed to achieve this goal.

At present, commercial scrubbing processes for the bulk removal of acid gases from raw process gas such as synthesis gas include MDEA, Selexol, and Rectisol. Most of these processes operate at less than about 95°C, although some can be designed to operate up to about 230°C.

Research is underway to develop acid gas removal processes capable of operating at temperatures up to 650°C; for example, the zinc-ferrite process is being developed by the DOE Morgantown Energy Technology Center. Ceramic membranes could be developed to operate at conditions close to the exit gas conditions from typical entrained flow gasifiers. Satisfactory operation under these adverse operating conditions would significantly improve coal conversion process economics and could lead to the recovery of the acid gases in sufficiently pure form for subsequent conversion to marketable products.

#### 3.1.7 Piping and Transfer Lines

Carbon steel piping lined with intermediate-purity (~55%) alumina, calcium aluminate cement castable refractory has performed well for large off-gas piping interconnecting the gasifier and the various gas quench, heat recovery and char removal components. Such construction will probably be used for similar applications in commercial plants.

#### 3.1.8 Raw Gas Treatment

Downstream of the gas quench, the process steps of CO shift, fine particulate and acid gas removal and methanation are generally familiar to petrochemical and ammonia producers. The selection of materials of construction for these systems in commercial plants is expected to follow rather well-established criteria and practices.

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## 4. HEAT ENGINES

### 4.1 TECHNOLOGY STATUS AND MATERIAL NEEDS

Two Fossil Energy subprograms in which materials are a significant consideration include:

Gas Turbine Systems. The goal is to develop the technology for firing turbines with coal, coal-water mixtures, or coal-derived fuel gases.

Diesel Engines. The goal is to develop the technology for firing diesel engines directly with coal, coal-water mixtures, or coal-derived fuels.

The AR&TD Materials Program is developing advanced ceramic materials, high-temperature alloys, and both the technical understanding and materials to combat wear, erosion, and corrosion problems in these systems.

#### 4.1.1 Coal-Fired Turbine Technology

The proposed coal-fired turbine system must compete with gas-fired turbines. Gas turbines with combined steam cycle systems were installed at a rapid rate during the late 1960s, before the rapid rise in oil and gas prices. They are modular and available in many sizes to fit a variety of applications, but 100 to 150 MW(e) installations are popular. Typical installed costs are \$300-400/kW with a 3-year lead time. The obstacle to growth of natural gas-fired turbine usage is instability in fuel prices.

If a coal-fired turbine were available, it could impact the combined cycle power generation, repowering, industrial cogeneration, and transportation markets. The coal-fired turbine might be achieved either by converting coal to clean liquid or gaseous fuel to feed a combustor, or by directly firing a combustor with coal-water slurry or finely ground coal powder. The present Coal-Fired Turbine Program includes developing turbine systems fired either by a cleaned hot-gas stream from a gasifier, or by finely ground, cleaned coal powder. The critical issues that are recognized are grouped as: (1) fuels selection; (2) combustion phenomena, including combustor and fuel performance to yield complete combustion that is necessary to achieve

system performance goals and to avoid corrosion, erosion, and deposition on turbine blades; (3) fuel-engine interactions, the tradeoffs required to limit to acceptable levels the corrosion of the turbine and heat recovery steam generator materials by alkali, sulfates, and other coal ash contaminants; deposition of adhesive ash onto turbine blades, and erosion of turbine components by abrasive ash particles; (4) control of sulfur and nitrogen compounds and particulates to meet emissions standards; and (5) systems integration to define the most cost-effective system possible.

Four cost-shared contracts totalling over \$75M were awarded to General Electric (GE), General Motors (Allison), Solar Turbines, and Westinghouse for development work through proof-of-concept testing. Of these vendors, only GE elected to use a conventional annular aircraft combustor configuration that restricts what can be done to clean the combustion gases; GE is no longer active in the program. The other three vendors are all exploring separate combustor/gas cleaning/heat recovery systems ahead of the turbine. The materials problems associated with producing clean, hot-gas streams have been discussed in Chapter 3: a considerable amount of materials development work is indicated. The current status of the major programs is summarized below:

(a) GE has experimentally verified that calcium-based compounds capture sulfur and has run an LM500 gas turbine simulator on coal-water mixture (CWM) for 23 h with less nozzle blockage than results from burning residual fuel oils. In addition, the annular metal-wall combustor achieves over 99% efficiency and deposition is reduced by adding kaolin aluminosilicate clay to the CWM.<sup>1</sup> Turbine nozzle blockage had been a problem in early tests and was originally solved by on-line cleaning and reduced vane temperatures, methods that are unacceptable for commercial operations.

(b) Westinghouse has designed and constructed a subscale slagging combustor. It features an oxygen-rich combustion stage, sorbent injection, impact slag separation, and a lean burning stage that produces gases low in  $\text{NO}_x$  at a suitable turbine inlet temperature. Westinghouse has found that emathlite is effective in reducing alkali in the hot-gas stream.<sup>2</sup>

(c) Solar's system is aimed at the industrial cogeneration market. Three subscale combustor designs have been tested, and dolomite injections to absorb sulfur have been demonstrated. Initial tests of the two-stage combustor with first-stage four-vaned turbine nozzle segments in place resulted in blockage of the vanes after less than 10 h.

(d) Allison is developing a combustor with a rich burning zone followed by a water quench, inertial (centrifugal) separation of particulates, and a lean zone.

#### 4.1.1.1 Materials R&D for Coal-Fired Turbines

The current projects involve materials research and development for two distinctly different zones of the turbine system: first, the relatively high-temperature, oxidizing region of the combustor; and second, the lower-temperature, reducing region of the turbine. These zones are separated by gas cleanup and particulate removal operations that are unique to each of the projects.

Combustor: Testing of commercially available materials of construction for the combustor, particularly refractory materials, is in progress, either in separate test programs or by exposure of materials in prototype combustors. The experience and data base developed for coal gasification by the AR&TD Materials Program from the mid 1970s to the mid 1980s has relevance to these conditions.

Gas Cleanup: System testing to determine the allowable levels of particulates and chemical impurities is in progress. While cyclones are the current devices of choice, some types of filtration and gas separation devices to operate at elevated temperatures may be needed. The AR&TD Materials Program currently features development projects on ceramic filters fabricated by chemical vapor infiltration of fiber bodies and work on ceramic membranes for high-temperature gas separations. Work sponsored by Morgantown Energy Technology Center at Oak Ridge on filter tubesheets and gas separations materials is directly relevant.

Turbine Components: The turbine inlet temperatures of the current programs are equal to or less than those of current land-based turbines, rather than the higher temperatures reached in aircraft turbines. Erosion and/or corrosion of airfoil materials and internal

parts is a major problem due to the gaseous impurities, erosive particulates, and mineral ash deposits of the coal-derived gas streams. Work is in progress to develop sorbents for gaseous impurities that in turn increase the solids loading of the gas stream that lead to increased emphasis on gas stream cleanup. The extent to which turbine materials development work will be required will depend on the success of these efforts. However, all projects provide for development of a suitable data base on degradation of turbine materials and any subsequent materials development work that may prove necessary. Protective coatings are standard within the industry, and their evaluation in the environment is anticipated.

The Electric Power Research Institute examined the case for power production by combined-cycle gas turbine-steam turbine systems using very clean gas produced by an advanced coal gasification process.<sup>3</sup> They concluded also that the commercialization of land-based gas turbines is extremely sensitive to economics, and in part dependent on the development of land-based gas turbines with high efficiency and capacity. Current commercial aircraft gas turbines operate at a maximum burner discharge temperature of about 1538°C (2800°F), whereas land-based gas turbines operate at 1204°C (2200°F). The increased efficiency of operating a land-based turbine at 1427°C (2600°F) may be critical to the economics of the situation. While there are differences in the service conditions and performance requirements for land-based and aircraft turbines, modification of land-based turbine technology to take advantage of available or near-term improvements should be pursued. This includes, on a component-by-component basis:

Compressor: Increasing compression ratio leads to higher temperatures and stresses in airfoils, and a need for higher strength materials.

Combustor: Achieving 1427°C (2600°F) turbine inlet temperatures will require advanced materials and cooling technologies, including advanced thermal barrier coatings, ceramic composites, oxide-dispersion-strengthened alloys, and fabrication techniques allowing improved cooling.

Turbine Airfoils: Achieving 1427°C (2600°F) turbine inlet temperatures will require improved cooling and higher strength alloys,

probably directionally solidified or single crystal airfoils. Protective coatings will be needed to provide oxidation resistance for longer lifetimes than are needed in the aircraft industry, while thermal barrier coatings on both stationary and rotating airfoils can reduce thermal stresses and increase turbine efficiency. Advanced fabrication methods (for instance, joining separate airfoils and shroud castings) may be required for cooling. Manufacturing large last-stage blades from high-temperature alloys may be challenging.

Turbine Disks: Stronger turbine disks, probably of nickel alloys that will require protection from sulfur capture upsets, will involve larger castings of these alloys than is current practice, and establishing mechanical properties and nondestructive examination technology.

Turbine Seals: The outer air seal clearance is critical to efficiency, at the rate of 1% fuel consumption/0.508-mm (0.20-in.) gap. Aircraft style abradable seals and thermal-barrier-coated seals may be needed.

Life Prediction: Life prediction methods that account for time, environment, temperature, and duty cycles should be developed. The development projects of the AR&TD Materials Program include advanced ceramic composite materials, improved austenitic alloys, and aluminides that should be directly applicable to some of these critical turbine components. The electrospark deposition process deposits wear-resistant materials of exceptional durability and corrosion resistance that may find application in turbines. The understanding of erosion processes that is supported by the AR&TD Materials Program is aimed at the turbine vane problem, and the ceramic composites under study appear promising as structural materials for future turbine applications.

#### 4.1.2 Diesel Engine Technology

Rudolph Diesel's early experiments were followed by other technically successful experiments between 1911 and 1940 in which some 19 experimental engines were tested on coal dust with 1 to 154 L/cylinder at speeds from 160 to 1600 rpm. The technology was abandoned because of severe wear rates from accumulation of char/ash paste on cylinder liner walls and in the oil. In the late 1970s, DOE Conservation and

Renewable Energy tested coal-water mixtures (CWM) with excellent mechanical results, but marred by a 50 to 75 times increase in ring wear rate and a 10 to 20 times increase in cylinder liner wear rate compared to oil-fired diesel engines. DOE Conservation and Renewable Energy has supported the development of an adiabatic diesel engine that required the application of ceramics for high-temperature engine parts.

Research in coal-fired diesels is driven by engine thermal efficiencies of 35 to 40% typical (that can reach 42 to 53% depending on bore size), with further increases to 50% typical (with potential for reaching 60 to 70%) by adding superchargers and bottoming cycles. From the user's standpoint, diesels are compact modules with good load-following capability, quick startup and shutdown characteristics, and low (~\$250/kW) capital cost.

The markets are substantial: about 40,000 utility, industrial, railroad, and marine diesels currently consume DF2. The available railroad market burns about large quantities of DF2 annually. The potential for coal-fired diesels in the trucking and automotive industries is staggering, but difficult to imagine because of engine complexity to satisfy environmental emissions concerns. There are three technical areas needing major improvement for coal-fired diesels to become commercially viable: combustion, engine wear, and emissions.

#### 4.1.2.1 Materials R&D for Diesel Engines

Materials technology and improvements coupled with design improvements to reduce engine wear are critical. The current program is aimed at a 2-year engine overhaul schedule, rather than the 4-year schedule common for DF2. Materials and materials-related work is in progress in the following critical areas:

Fuel Pumps: Conventional fuel pumps have been evaluated and found to wear at unacceptably high rates. Current work is aimed at finding materials of construction that are compatible with both existing and advanced fuel pump designs.

Fuel Nozzles: The current generation of steel nozzles that suffice for service have been demonstrated to be unsatisfactory for CWM fuel. Ceramics, ceramic composites, cermets, and other special materials are currently under evaluation. Some consideration is also being

given to special coatings. Design is critical in nozzle material selection.

Cylinder Liners and Rings: Particulate material causes three-body abrasion that is sensitive to stroke parameters and lubricants. Testing of wear-resistant materials and protective coatings is in progress.

Exhaust Valves: High velocity exhaust gases laden with ash cause rapid wear of valves made of conventional materials. Wear-resistant materials and coatings are being evaluated for this service.

Turbocharger: Exhaust gases are used to drive a turbocharger. The vanes are subject to rapid wear when constructed of conventional materials. Evaluation of wear-resistant materials and coatings suitable for this service is in progress.

Oil-Lubricated Components: Blowby past the rings contaminates the engine oil with abrasive particulates. Effective filtration of the oil is being evaluated that may require improved filter materials and filtration systems.

Materials may also be a consideration for meeting emissions requirements. At 96% combustion efficiency, a 1% ash coal should produce 318 g (0.7 lb) of ash and 1043 g (2.3 lb) of unburned carbon per million Btu. Modifications of ceramic bag filters, cross-flow filters, and candle filters that are currently being developed for hot-gas cleanup applications in coal gasification may prove useful for this service, and coordination of the work is handled through program management. The AR&TD Materials Program is developing advanced ceramic composite materials, improved austenitic alloys, and aluminides that may prove useful in several of these areas. The electrospark deposition process may prove valuable in depositing high quality protective coatings on rings, cylinder walls, and other wear surfaces. The Tribology Department of the National Institute of Standards and Technology is supported on a wear project that is directly interfaced to this problem, and is examining the particulates responsible for wear in engine tests. The understanding of erosion processes that is supported by the AR&TD Materials Program is directly applicable to damage to valve and supercharger turbine rotors, areas where ceramic composites may be directly useful.

#### 4.1.3 Nondestructive Testing

Nondestructive examination (NDE) techniques for materials characterization and flaw detection can have a large cost impact if applied to green-state ceramic bodies before densification. Correlation of flaw data (size, type, and location) and characterization (density distribution, porosity distribution, binder/plasticizer distribution, elastic modulus variation, etc.) should lead to better failure prediction models. Nondestructive examination methods may also be used to inspect raw powders before each processing step to identify which step is introducing flaws. Characterization of microstructure (grain size, porosity, free silicon content) can also be related to processing parameters as well as component performance and may lead to better predictions of lifetime. However, the NDE effort should be directed not only to green-state specimens but to densified specimens as well. Also, laboratory specimens and actual components used in heat engines<sup>1</sup> and heat recovery systems (e.g., turbine blades, piston caps, valve covers, valve wear plates, and heat exchanger tubes) should be studied by NDE together with a rather comprehensive fracture behavior effort. The type of defects to be detected by NDE is dependent upon whether the ceramic material is a monolithic material or a composite material, whether surface or bulk body is the most important, and whether the material is in a green or densified state.

The allowable load on structural ceramics is controlled by the stress necessary to propagate a suitably oriented and sized flaw to critical size. This critical flaw size may be as small as 10  $\mu\text{m}$ , which is about two orders of magnitude smaller than those for metals, and special techniques must be developed to detect such small flaws. Most ceramic materials are subject to slow crack growth. In principle, the probability of failure can be predicted if the temperature, stress, and atmosphere are known; if the material is adequately characterized; and if the type and size of existing flaws are known. If it can be established that flaws are smaller than a determined critical size and that the material properties and slow crack growth behavior are known, component life can be assured. The resolution and speed of such NDE measurements must be improved. Component reliability must ultimately

be assured by developing controlled processes for fabricating components and by keeping the manufacturing process in control. NDE examination is an integral element of such a quality program and is preferable in terms of efficiency, cost, and quality to a program that depends on mass inspection and rejection of significant numbers of components.

#### 4.1.3.1 Densified Ceramics

Process-induced defects, such as inadequate binder distribution or lack of uniform green density, embody themselves in the final product. Other flaws to be detected typically include high- and low-density inclusions, cracks, and large voids. In composite ceramics made with random-length, random-oriented fibers (whiskers), typical flaws to be detected include whisker clusters, whisker stratification, and inclusions. In both monolithic and composite ceramics, where large loads are carried, measurement of residual stress levels in densified parts is also desirable.

The best technical NDE approach for the ceramic material depends on whether the material is a composite or a monolithic, if surface or whole-body flaws are most important, and if the material is in the densified or green-body state. Application of ultrasonic techniques to densified ceramics allows higher frequencies (>200 MHz) than those allowable for green-state ceramics. Higher frequencies and thus shorter wavelengths provide for improved spatial resolution, which is necessary for detecting critically sized flaws in the whole body.

Use of focused acoustic transducers with appropriate signal processing should allow complete through-the-body flaw detection (and characterization) such that only selected planes in a body could be interrogated.<sup>3</sup> The spatial resolution capability has yet to be determined. Special highly focused transducers may allow resolution in the 25- $\mu\text{m}$  range for specific types of defects.

Radiographic techniques (X- and gamma-ray computed tomography, X- and gamma-ray contact and projection, real-time, and film with image processing) also hold potential for interrogating densified ceramic bodies. It has been known for some time that low-kV radiographic imaging techniques are best for low-density materials.<sup>4</sup> Ellingson,

Roberts, et al.,<sup>5</sup> have shown that for green-state ceramics, X-ray heat voltages less than 50 kV (photon energies ~20 keV) can be used; but for densified, reasonable sized specimens with high-atomic-number material, up to 1-MeV photon energies are necessary for penetration. Highly tailored radiographic techniques do appear to hold promise for inspecting ceramic materials.

Computed tomography<sup>5-9</sup> (CT) can detect low- and high-density inclusions and cracks in the 25- to 50- $\mu\text{m}$  range in quite large bodies, and it can map density distributions. The energy levels needed for CT imaging depends on the composition of the ceramics, the thickness, and the state (green or densified). An important attribute of CT is that it provides a method to interrogate the entire ceramic body in a noncontacting way and provides almost immediate images on which to base decisions. The limits of operation for flaw detection and characterization must be defined, and the cost of implementation must be reduced.

Contact or projection radiographic imaging has strong potential for application to ceramics. Its drawback is that no through-thickness spatial information is provided, and two-dimensional flaws normal to the beam are not detected. Thus, a high-density inclusion may be detected, but the method does not allow the location (within the thickness dimension) in the body to be determined. For thin parts, location in the thickness may not be important, and thus the image may be immediately useful. Analysis of X-ray images by digital image processing techniques will allow isodensity maps to be obtained as well as enhancement of low-contrast defects such as silicon inclusions in silicon-based ceramics.

Surface acoustic waves may be useful for detection of surface flaws, such as machining-induced cracks, by use of backscattering examination. Backscattering may also be useful for characterizing surface finish (i.e., machining-induced roughness).

Small-angle neutron scattering, a new NDE technique, may be used to detect micropores and/or residual stresses. In general, studies must be carried out to establish the correlation between results of the various NDE studies.

#### 4.1.3.2 Green-State Ceramics

For green-state ceramics, it is desirable not only to detect flaws such as agglomerates, inclusions (iron, silicon, etc.), voids, and cracks, but to characterize the specimens for density distribution, binder content and distribution, and porosity distribution. The delicate nature of green-state bodies implies that noncontacting methods be used. In addition, full-volume interrogation is necessary because it is not sufficient to look only at surface flaws.

In contrast to densified materials, where all chemical additives (binders, plasticizers, and sintering aids) have been burned out, green-state ceramic bodies still contain these additives. The distribution of these additives affects the distribution of the mechanical properties within the ceramic part. Thus, in addition to acoustic and radiographic techniques discussed earlier for densified ceramics, chemically sensitive NDE methods such as nuclear magnetic resonance (NMR) may have potential for application. Full-body mapping of porosity, distribution of carbon-containing binders/plasticizers, and perhaps silicon distribution in siliconized  $\text{Si}_3\text{N}_4$  may be possible.<sup>10</sup> For mapping of porosity, dopants that are compatible with the additives but that have nuclear spins (i.e., the nuclei are detectable by NMR) may allow mapping of porosity. Perhaps green-body characterization is where NDE could offer the highest payoff in ceramic processing.

Present techniques most widely employed by industry for NDE of ceramics are X-ray radiography and fluorescent dye penetrant testing. These techniques provide a relatively coarse resolution of discontinuities (density variations, pores, cracks, inclusions, etc.). However, as noted earlier, efforts are under way to advance NDE techniques for structural ceramics. The techniques being studied include advanced acoustic methods (including focused transducers and signal processing), X- and gamma-ray tomography, X- and gamma-ray radiography with digital image processing, NMR imaging, surface acoustic wave testing, small-angle neutron scattering, and overload-proof testing. No single technique is expected to serve as a universal flaw detection and characterization method. Several techniques will be required to assess ceramic components thoroughly and cost-effectively in the green and densified states. Most of these techniques are currently being

evaluated by the Fossil Energy AR&TD Materials Program and have application to heat recovery systems as well as heat engines.

Future studies should focus on selected structural ceramic specimens ( $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{ZrO}_2$ , and  $\text{Al}_2\text{O}_3$ ), including samples in the green state. Samples should have variations in shape as well as variations in microstructure (grain size, grain distribution) and flaws (seeded inclusions, cracks, and pores).

Work on ceramics should include establishing the ability to characterize green-state bodies. This ability would affect not only ceramic process development but flaw detection as well. Variations in ceramic specimen parameters relative to flaw detection should be used to predict fracture behavior in laboratory specimens (tensile and flexure stress modes), and the relationship between flaw detection and failure needs to be established. Fracture mechanics analyses and microstructural evaluation should be carried out to identify flaws most likely to limit component life so the NDE effort can focus on the most important areas. Studies must be carried out to correlate NDE results with fracture behavior to establish the utility of the NDE techniques. Tests must be performed on samples with controlled flaw populations to determine the effect of flaws on failure probability distribution. A significant effort should be developed to evaluate CT, acoustic, and NMR imaging for ceramics in the green and densified state, and to correlate the data with fracture behavior. Cracks, porosity, and density variations are all potentially detectable with these advanced sophisticated methods. In addition to CT scanning, advanced NMR imaging systems for materials should be evaluated.

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## 5. COMBUSTION SYSTEMS

### 5.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

#### 5.1.1 Fluidized-Bed Combustion

The combustion of coal in a fluidized bed of crushed limestone or other sulfur sorbent offers a more energy-efficient approach for sulfur capture than is currently attainable with other more conventional combustion processes. When coal is burned in a fluidized bed, the bed temperature must be kept below about 950°C to prevent ash agglomeration. In fact, efficient removal of sulfur will probably limit the bed temperature to below 900°C; these relatively low combustion temperatures also limit NO<sub>x</sub> emissions. The heat of combustion may be transferred to in-bed and above-bed tubes carrying water, steam, or air, or it may be removed by increasing the air flow to greater than that required for stoichiometric combustion. In the latter application, the bed is normally pressurized, and the combustion gases are expanded through a gas turbine. Although the tube temperatures of the in-bed heat exchangers vary greatly with choice of coolant, the heat exchanger concepts are alike in their requirements for uncooled support members, coal ports, ash lines, and other components that can operate at temperatures approximately equal to the bed temperature.

Materials requirements for fluidized-bed combustors (FBCs) have been addressed in several design studies.<sup>1-3</sup> All components contacted by the fluidized bed - heat exchanger tubes and supports, air distributor plate, coal and limestone feed nozzles, side walls, bed-drain hardware, and instrumentation - must satisfy operating requirements that are unique in terms of past operating experience for coal combustion systems. Design parameters, such as location of coal feed ports and air fluidizing velocities, strongly affect materials performance and the compromises that can ultimately be achieved to establish the feasibility of FBC concepts. Additional challenges to the designer are problems of creep and fatigue arising from imposed loads and vibrations. Not unique, but also of concern, are problems with dissimilar-metal welds.

Fireside corrosion of superheaters in conventional pulverized-coal-fired boilers is due to the deposition of ash-containing alkali sulfates on the metal. Sulfate-containing coatings are also formed on heat exchanger and other metallic surfaces immersed in fluidized-bed combustors using limestone as a sulfur sorbent above approximately 400°C. In this case, the coatings are predominantly  $\text{CaSO}_4$ , which remains solid even at the maximum bed temperature. Nevertheless, chemical interaction between these coatings and the underlying metal-metal oxide substrate is a major factor in the corrosion of FBC materials. Also of importance is the distribution of air, coal, and combustion gas within the bed. Determinations of the oxygen fugacity of the bed by solid electrolyte probes responsive to oxygen anion activities show rapidly fluctuating oxygen pressures at any given point in the bed, the pressures reaching apparent levels as low as  $10^{-10}$  Pa, implying that transient reducing conditions exist in the vicinity of burning coal particles.

In addition to corrosion, the in-bed and freeboard heat exchanger components may also be subject to erosion. In practice, the local gas velocities in the freeboard (above-bed) area of an FBC are comparable to those in conventional coal-burning systems. Thus, although the particle size and density are much higher in the FBC, problems with erosion in the freeboard region appear to be more conventional than those in the bed. Erosion patterns in the in-bed regions of fluidized beds have been of two general types. In the first type, tube surfaces and water walls operating at temperatures lower than approximately 300°C in some (but not all) fluidized beds have suffered rapid erosive and abrasive wear. The eroded surfaces appear highly polished, exhibiting no oxide films, sulfate, or char coatings. The second type of erosion has been manifested at higher temperatures (400 to 600°C) where the under surfaces of heat exchanger tubes have sometimes exhibited much higher wall losses than the mating upper surfaces. The latter form of erosion appears to be associated with an erosive effect on  $\text{CaSO}_4$  deposits and/or underlying oxide films. Neither form of erosion has been observed for heat-resisting (austenitic) alloys operating at 800°C or above, where relatively thick, wear-resistant

oxide films are formed. Three factors that appear important in effecting in-bed erosion are: (1) the feedstock characteristics such as chemical composition, particle size and size distribution, and hardness; (2) the operating conditions such as fluidizing velocity, temperature, and pressure; and (3) the mechanical design of the combustor including the tube bundle dimensions of tube diameter and pitch, the distance from air distributor and coal and limestone introduction points, and the materials of construction of tubes and support hangers. The complex interaction of these variables determines the nature of fluidization, the combustion gas composition, the possible formation of protective deposits or excessive corrosion, and, finally, the rate of erosion.

A recent overview of FBC erosion<sup>4</sup> indicated that several additional (to those discussed above) mechanisms may operate in FBCs, although not at all times or in all units, including the following: groups of particles moving against tubes under the influence of gas bubbles and solids in the vicinity of the group of particles; fast-moving particles in the wake of rising bubbles; large, though slowly moving, particles with high kinetic energy; particles thrown into metal surfaces by the action of bubbles collapsing; particles accelerated into in-bed components under the influence of in-bed jets associated with coal and limestone feedports, limestone recirculation ports, and air streams used to keep bed drains clear of obstructions; and particles trapped within and moving with large-scale flow patterns in the fluidized bed. Bed design parameters, particularly the nominal fluidizing velocity, the design of the air distributor and lower bed plenum, and bed depth are fundamentally important in controlling erosion.

In general, combatting in-bed erosion through material upgrading and coating has not been as effective as have controlling local particle velocities and using spoilers for disrupting adverse solids flow patterns. Erosion problems of still another form are encountered when the combustion gases from the FBC are expanded through a gas turbine. A substantial amount of work has dealt with gas turbines ingesting dusty air and with the recovery of energy from fluidized-bed catalyst regeneration units by expanding the product gas through turbines. All

this work indicates that even moderate concentrations of 5- $\mu\text{m}$  particulates can be very damaging at the high velocities in the engine. Because these erosion problems cannot be solved by materials selection only, design solutions must also be sought. The magnitude of the erosion problem is strongly influenced by the degree of hot-gas cleanup that can be realized and by the detailed aerodynamics of the turbine. The degree of hot-gas cleanup strongly influences the particulate concentration, and the aerodynamics control particle velocities and temperatures in multistage gas turbines. Finding a solution to the coupled hot gas cleanup and gas turbine erosion problem is probably the most challenging technological problem facing the pressurized fluidized-bed combustion (PFBC) system.

Erosion and deposition (fouling) have generally limited the lives of coal-fired gas turbines. However, at longer times or higher temperatures, hot corrosion of gas turbine components appears to be a significant threat.<sup>5</sup> After entering the turbine, the PFBC gases are cooled by expansion in the turbine and by contact with cooled metal parts or with the boundary layer surrounding them. Alkali sulfates can then condense on the metal surfaces. Thus, the selection of the metal temperatures controls not only the rate of the corrosion reactions but also the rate of deposition of corrodent on the surface. Although the alkali vapor concentrations produced in a PFBC are in most cases lower than those encountered in pulverized-coal combustion systems, the flux of alkali salts in the gas turbine will be substantially greater than that regarded as acceptable for current engines using distillate fuels. Temperature is critically important, and there is now strong evidence that corrosion of PFBC turbine components will be even more severe in the range 600 to 750°C than at higher temperatures. However, some alloys and claddings are clearly less susceptible to this type of attack than are others, and the choice of an adequate turbine protection scheme (material and surface temperature) is not yet clear.

Given the complexity of materials degradation processes in fluidized beds (e.g., erosion, corrosion, and erosion/corrosion), it is not surprising that the wastage rates reported for specific heat exchanger materials have differed by orders of magnitude among the

various in-bed materials studies conducted to date.<sup>6-8</sup> However, the pattern of materials behavior has become more predictable as specific degradation mechanisms have been identified. For example, at service temperatures of 800°C and above, candidate materials have narrowed to austenitic stainless steels (including Alloy 800), and the degradation of these materials is controlled by classic oxidation/sulfidation mechanisms. The major concern with these materials is breakaway oxidation, which is associated with a critical distribution of internal sulfides near the oxide-metal interface. Still to be determined is the role of CaSO<sub>4</sub> deposits in the corrosion processes and the transport mechanisms of sulfur through the oxide film. Under steam boiler conditions (600°C and below), degradation of candidate heat exchanger materials has been negligible except where erosion has accelerated the normal oxidation processes or abraded unoxidized tube surfaces.

Although laboratory corrosion and erosion tests are extremely useful in establishing the environmental and temperature conditions under which a given degradation mechanism can operate, it is still necessary to relate these laboratory test results to fluidized bed design parameters (excess air and SO<sub>2</sub> in the flue gas, bed temperature, superficial velocity, sorbent-fuel ratio, coal and sorbent feed size, etc.). Such comparisons require the exposure of materials in an FBC dedicated to materials testing, where the corrosion performance of heat exchanger and turbine materials can be correlated with bed design and operating parameters.

Laboratory experiments under carefully controlled conditions are being conducted to understand the mechanisms and microstructural conditions that lead to breakaway oxidation at 593 to 850°C. Recent studies on heat exchanger materials exposed at 1140°C to an alternating high-P<sub>O<sub>2</sub></sub>/low-P<sub>O<sub>2</sub></sub> atmosphere with a cycle time of 10 or 100 h showed that the materials need a sustained exposure for times greater than 10 h to low-P<sub>O<sub>2</sub></sub> atmosphere to initiate sulfidation attack.<sup>9</sup> It has also been established that a combination of CaSO<sub>4</sub> or CaO deposits and the presence of low P<sub>O<sub>2</sub></sub> in the gas phase can lead to initiation of sulfidation in high-chromium alloys.<sup>10</sup> Tests at lower temperatures should be conducted

to establish the conditions under which erosion will affect the mechanical integrity of oxide films and  $\text{CaSO}_4$  deposits. Laboratory tests are also required to identify the mechanisms of low-temperature hot corrosion of turbine alloys and coatings in simulated PFBC flue gas environments.

The materials requirements for certain hot-gas cleanup systems, such as cyclones, do not seem particularly difficult to meet, although candidate materials should be subjected to long-term testing. However, more advanced hot-gas cleanup systems (e.g., ionic conducting materials) are under development; their materials requirements must be determined, and successful materials performance must be demonstrated.

A current problem in steam generators is that oxide scale spalls from reheater and superheater tube surfaces and partially obstructs passages or damages turbines. Conditions of high heat flux, such as in liquid-metal heat exchangers, increase the extent of spallation.<sup>11</sup> Because the heat fluxes of FBC in-bed steam generators will be higher than those in current fossil-fired generators, the problem of spallation could be accentuated. A program should be initiated to determine the effect of the heat fluxes in FBC steam generators on oxide spallation. If the effect is significant, the benefits of chromizing or substituting more oxidation-resistant materials should be evaluated.

Dissimilar-metal joints between ferritic and austenitic boiler tubes are currently made with high-nickel filler metal. Such joints may not be suitable for applications that locate the joints within the fluidized-bed region of atmospheric FBCs (AFBCs), because such high-nickel alloys are susceptible to catastrophic sulfidation corrosion. The performance of joints made by existing methods must be related to operating temperatures and local bed conditions in AFBCs, and, if necessary, alternative joining methods and materials must be explored.

Nondestructive techniques (ultrasonic and eddy current) for in-service inspection should be developed and applied for tubing, dissimilar metal welds, and other components.

### 5.1.2 Conventional Combustion

Relative to combustion systems, the two central objectives of the DOE Office of Fossil Energy are (1) substitution of coal (or coal-liquid mixtures) for oil and natural gas in utility and industrial boilers and (2) extension of the reserves of oil and gas by improving the reliability and efficiency of boilers and furnaces. Replacement of oil and natural gas by pulverized coal or coal-liquid mixtures in industrial and utility boilers requires solutions to several technical problems. The principal problems are those of fly-ash fouling, slagging, corrosion, and erosion of boiler tubes and other components in conventional combustors. These problems are caused in part by the mineral matter present in the feed coal and the transformation and reactivity of the mineral matter during and following combustion. An adequate understanding of the mechanisms responsible for the chemical and physical reactions seen with the use of coal or coal-liquid mixtures is needed. Tube wastage in conventional pulverized-coal boilers is caused primarily by the corrosive reactions that occur at high temperatures between the impurities contained in the coal and the metal tube surfaces. Low-temperature corrosion is due mainly to attack by sulfur-containing acids. In addition to the development of more corrosion-resistant materials for boiler components, better coal cleaning techniques (as discussed in Chap. 7) will result in the removal of a large amount of the ash and sulfur from the feed coal and, thereby, reduce the problems caused by these materials. In addition to providing a better quality coal for pulverized-coal combustion, improvement of feed coal quality is an important step in the preparation of coal-liquid slurries for combustion in retrofitted oil or gas combustors. The prime problems encountered when oil- or gas-fired boilers are retrofitted to burn coal or coal-liquid slurries are corrosion, erosion, and wear of the burner nozzle. Again, proper coal cleaning will reduce this problem somewhat; however, burners will need to be redesigned to atomize the injected slurries into the combustion zone properly. The coal-liquid mixtures most successful to date have been coal-water mixtures.<sup>12-13</sup> Currently coal-oil mixtures are not economically attractive compared with oil, and recent studies showed

that considerable loss of power-generating capacity could be expected when coal-oil mixtures are used in oil-fired boilers.<sup>12</sup> Slurry production also requires the addition of chemicals that cause a different type of fouling problem, and this area will need to be addressed as well before coal-water mixtures will replace oil or gas. However, the use of slurries resulted in NO<sub>x</sub> emissions 100 to 200 ppm lower than those occurring when pulverized coal of the same quality was burned.<sup>13</sup>

Among the current materials limitations that the Electric Power Research Institute (EPRI) has singled out as particularly significant to electrical utilities are the corrosion fatigue of steam turbine rotors and blades and the oxide spalling of superheater materials, which causes erosive impingement on turbine blades.<sup>14</sup> The attainment of higher efficiencies in the steam-Rankine power cycle demands materials with improved fireside and steam corrosion resistance at 600 to 700°C. Higher efficiencies are thus achievable by the substitution of more highly alloyed metals for present-day boiler materials, albeit with a significant increase in plant capital costs. The development of oxidation- and sulfidation-resistant coatings to upgrade existing boiler materials may be a more cost-effective means of achieving the needed temperature increases.

Failure of dissimilar-metal welded joints in steam generators has become a major factor affecting the reliability of utility steam boilers.<sup>15</sup> Superheaters and reheaters delivering steam at 540°C commonly employ austenitic stainless steels for higher temperature regions and ferritic steels for lower temperature regions. Although these tubes can be joined with a variety of welding approaches, cracks are characteristically encountered in the ferritic material adjacent to the weld interface or in the heat-affected zone. Of 54 utilities responding to a survey sponsored by the American Society for Testing and Materials, American Society of Mechanical Engineers, and The Materials Properties Council, 20 reported dissimilar-metal weld failures.<sup>15</sup> These failures involve 60 units of a total of 320 and were not attributable to poor welding techniques. Improved techniques were successfully developed in an EPRI-funded program for joining austenitic stainless

steels and ferritic tubes to resolve the cracking problem, and the reliability of steam power plants has been increased.

The effluent emission standards imposed by the Environmental Protection Agency on fossil-fueled power plants require the removal of  $\text{SO}_2$  from the stack gases of plants burning high-sulfur coals and fuel oils. The most common method for  $\text{SO}_2$  removal is wet scrubbing. Typically the stack gas is quenched by water immersion and is then passed upward through a spray tower in which a neutralizing material, such as limestone or  $\text{MgO}$ , is contacted with the gas to capture sulfur-bearing species. Wet scrubbers can use a variety of liquids, ranging from seawater to both acidic and alkaline chemicals. As these liquids contact the flue gas, the absorption of  $\text{SO}_2$  lowers the pH and increases corrosion. Chloride ions introduced by the coal, scrubber water, or sorbent also exacerbate the corrosion problem, especially where closed-loop recirculating water systems are used. The relatively low temperature of the combustion gas as it leaves the scrubber also poses a serious dew point corrosion problem (condensation of acids) in stack and blower sections downstream from the scrubber.

Corrosion problems experienced to date in the operation of pollution control equipment have been sufficient to warrant upgrading to more corrosion-resistant alloys to reduce downtime and repair.<sup>16</sup> Corrosion testing and field surveillance will be required to verify that the performance improvement in the upgraded materials is cost beneficial.

As noted above, the EPRI has instituted a materials development program to improve the reliability of steam turbine rotors and blades. Advances in turbine material performance require commensurate improvements in steam supply components. Duplex materials such as corrosion-resistant claddings on austenitic stainless steels, when retrofitted into existing steam generators, have proved very cost-effective in reducing fireside corrosion under current boiler operating conditions.<sup>17</sup> The claddings used in the latter application are generically similar to those being developed for gasifier applications. Accordingly, coating and cladding developments for gasifier applications should be extended to cover potential coal-fired boiler

applications at temperatures of 600°C and higher. Nondestructive techniques, including eddy-current, ultrasonic, and infrared methods, are needed to accommodate the cladding developments.

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## 6. FUEL CELLS

### 6.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

Modern fuel cells convert the chemical energy released by oxidizing a fuel into electrical energy at high efficiency, with some release of recoverable heat.<sup>1-4</sup> Simple cells consist of an ionically conducting liquid or nonporous solid electrolyte layer that separates porous, electronically conducting electrodes. Fuel and oxidant are supplied to the anode and cathode, respectively, migrate to the electrode-electrolyte interface, react, and produce waste products that migrate away from their respective sides of the electrolyte. Electrodes are current collectors connected through an external circuit in which electrons flow from the anode to the cathode. Cells are stacked (connected in series to produce useful voltages), provided with manifolded flow channels for reactants and products, and thermally controlled by various heat transfer means. Fuel cell systems precondition fuel and recover waste heat with a variety of internal and external devices.

Of the major current fuel cell (FC) types [phosphoric acid (PAFC), molten carbonate (MCFC), solid oxide (SOFC), solid polymer, and alkaline], Fossil Energy supports major programs for the first three and some research on solid polymer electrolytes, because they are most compatible with fossil fuels. These four cell types were listed in approximate order of readiness for commercialization; none has been demonstrated to be competitive with other options for electricity production, but together they offer future advantages for utility power, cogeneration, industrial, transportation, military, and space applications. Demonstration PAFC and MCFC systems have operated to over 10,000 h. New materials could dramatically alter the future of each type of fuel cell by improving its performance, fabricability, economics, compatibility with fossil fuel, or environmental acceptability. The AR&TD Materials Program now performs electrochemical materials research that could benefit the SOFC, and other ongoing

materials research - ceramics, aluminides, and advanced stainless steel alloys - could impact all systems. A project is ongoing to develop microwave sintering techniques for solid oxide fuel cells.

#### 6.1.1 General Materials Considerations

Most fuel cells share some common materials problems:

1. In all fuel cells, the electrolyte, mechanical supports, and the containment system are exposed to strong oxidizing and reducing conditions on the cathode and anode sides, respectively. There are few materials that resist degrading reactions in both oxidizing and reducing environments. Typically, materials are sought to function adequately for the operating life of the cell, perhaps 10,000 to 40,000 h, and survive upset conditions.

2. The porosities of both anode and cathode, necessary for material transport, generally result in physical weakness. Many stack designs depend on clamping forces to minimize physical migration (leaking, seepage, etc.) of some system component, and creep of the porous structures under load is a constant engineering problem.

3. Catalysts must be physically placed at an electrode-electrolyte interface. To be effective and inexpensive, they must be finely divided and anchored in place. Migration and coarsening of catalyst, corrosion of its support structure, and poisoning of the catalyst by its environment and fuel contaminants are serious problems needing improvement.

4. Elements that operate in a highly chemically active region in an electric field are subject to dissolution, electrically driven ionic migration and diffusion, and reprecipitation. Thin elements promote desirable low electrical resistance and materials costs, but also high field gradients and short diffusion distances with rapid migration and interdiffusion effects.

5. Cell stacks are closely integrated arrays of components that are subjected to thermal cycling, sometimes during construction, and nearly always during operation. Preventing failures from thermal expansion mismatch and thermal stresses requires delicate balances in both materials and designs.

### 6.1.2 Phosphoric Acid Fuel Cells

It is generally felt that PAFCs are sufficiently near commercialization that direct AR&TD Materials support is not appropriate. Demonstrating that economies of scale can make PAFCs competitive with other systems is clearly outside the Materials Program scope. Some inventions could dramatically improve their future potential, however, including the following materials-related considerations:

Fuel Preparation: Hydrogen is the only current fuel with sufficient mobility to operate PAFCs near 200°C. Hydrogen-bearing fuel gas can be made by externally reforming clean, coal-derived gases, naphtha, or natural gas. Either catalysts for reforming these hydrocarbon fuels or gas separation membranes to provide inexpensive fuel could markedly affect system economics. Efficient oxygen separation might also be useful.

Electrolyte: Liquid phosphoric acid is contained in a membrane such as polytetrafluoroethylene (PTFE)-bonded silicon carbide to retain electrolyte by capillarity. Built-in reservoirs for electrolyte replenishment and design for electrolyte retention retard long-time cell voltage degradation; further improvements are possible.

Anode: Hydrophobic electrodes to minimize acid migration contain platinum catalyst in porous graphitic papers or felts bonded with PTFE (wetproofed). Micropores below 50 Å in diameter give high reaction surface area while 3- to 50- $\mu\text{m}$ -diam pores distribute gas; other systems have been explored. Gas barrier layers can be formed by trapping liquid in a fine-pore-size layer. Platinum electrocatalyst materials are poisoned by H<sub>2</sub>S, CO, and S above some levels. While low-loaded platinum systems that will tolerate 1.5% CO and up to 50 to 75 ppm (H<sub>2</sub>S + COS) are known, less expensive catalysts are desired. Particulate binding of electrode pore structures is poorly understood but may become a problem for coal-derived fuels.

Cathode: Corrosion-resistant, inexpensive graphite supports and improved catalysts are needed for cathodes. Catalyst substrates of acetylene black or graphitic materials are already near their limits of corrosion resistance on the cathode side. Alternate ceramic support

materials have been explored, including high-surface-area titanium carbide, silicon carbide, and tantalum carbide. Electrocatalytic reduction of oxygen at about 0.4 V overpotential is costly in terms of efficiency; an affordable catalyst with acceptable kinetics at lower overvoltage is highly desirable. Platinum alloys, organometallic catalysts, and novel platinum catalysts are all possibilities.

Structural Members: Structural members have an important impact on cell economics because the current choices are not compatible with increasing temperatures and pressures above the 205°C and 8 atm level to increase cell voltage. PTFE, the material of choice for corrosion resistance, does not have sufficient creep strength, and alternatives are needed where it is used. Separator plates inexpensively molded from graphite-resin mixtures and carbonized at 900 to 1200°C are not sufficiently corrosion resistant, and the corrosion-resistant fully graphitized material heat-treated at 2000 to 2900°C is too expensive for increased temperatures and pressures. A major innovation is required to circumvent this dilemma in oxidizing regions, such as waterproofing inexpensive materials or doping graphite.

### 6.1.3 Molten Carbonate Fuel Cells

MCFCs presently offer higher system efficiencies than PAFCs, but are further from commercialization. MCFCs can use coal-derived fuels directly, unlike PAFCs: they are not poisoned by CO and consume CO as fuel through a water-gas shift that produces H<sub>2</sub>. Integrating a MCFC with a coal gasifier and using the rejected heat for a bottoming cycle or for industrial cogeneration is one of the most promising coal-based technologies for electric power generation, with projected system efficiencies over 50%. Increasing operating pressures to 10 atm increases reversible cell voltage, reduces polarization voltage losses, and increases gas solubilities (hence power densities or voltages). Some areas in which generic materials improvements would advance the technology include:

Fuel Preparation: At the 650°C operating temperatures of MCFCs, nickel catalysis for external or internal steam reforming of hydrocarbon fuels is feasible; contamination-resistant catalysts for coal-derived gases are needed. H<sub>2</sub>S chemisorbs on Ni catalyst surfaces and

blocks active sites, poisoning the catalyst for the water-gas shift reaction. Membrane or electrochemical materials for contaminant removal are another alternative.

Electrolyte and Electrolyte Matrix: Numerous carbonates form highly conductive liquid phases that can be retained by capillarity forces in porous solids in a layer between the electrodes. The most common are 62% Li-38% K, 50% Li-50% Na, and 50% Li-50% K. Varying base compositions and additives can change corrosivity, cathode reaction kinetics and solubility,  $\text{LiAlO}_2$  matrix stability, and electrolyte migration. Basic data on solubilities, diffusivities, equilibrium constants, and rate constants are generally not available.

Migrating electrolyte damages other cell elements, makes sealing difficult, and reduces cell performance. There is no known substitute for nonwetting PTFE (used in low-temperature aqueous electrodes) to prevent electrolyte migration at MCFC temperatures. Paste electrodes of mixed carbonate and fine  $\text{MgO}$  or  $\text{Al}_2\text{O}_3$  have been replaced by low-density, porous, sintered ceramic ( $\text{LiAlO}_2$ ) matrices with controlled pore sizes that are mechanically weak and subject to cracking, particularly from volume changes during carbonate phase transformations (melting). The magnitude of this problem depends on system design and electrolyte matrix design, but crack arrestors and microstructural control are important. Fired lithium aluminate with controlled porosity may be incorporated between the matrix and the anode to prevent carbonate migration, system deterioration resulting from electrode cracking, and gas crossover as electrolyte is lost from the matrix.

$\text{H}_2\text{S}$  in coal-derived fuels oxidizes to  $\text{SO}_2$  that reacts with carbonate ions in the electrolyte; these reactions are reversed by burning clean fuel, so periodic off-normal cleanup may be possible. Membrane or electrochemical gas cleanup mechanisms would be valuable.

Anode: Cell reaction kinetics at  $650^\circ\text{C}$  allow nickel catalysts rather than expensive precious metals. Sintered nickel anodes are typically 60 to 70% porous, with a 4 to 6  $\mu\text{m}$  pore diameter to prevent carbonate migration from the electrolyte matrix. At  $650^\circ\text{C}$ , however, pure nickel sinters and deforms readily over a 40,000-h cell design

lifetime, creating difficulty in maintaining the sealing forces and electrical contacts. Nickel-chromium and nickel-aluminum alloys and metal-coated ceramics ( $\text{LiFeO}_2$ ) have been explored as alternate materials. Improved materials are still needed.

Solid particulate contaminants in coal-derived fuels can block gas passageways and the anode surface when they exceed roughly 0.1 g/L of particles over 3  $\mu\text{m}$  in diameter. Carbon deposition can be avoided by maintaining a  $\text{H}_2\text{O}$  partial pressure in the gas stream that preferentially forms methane. Perhaps 10 ppm  $\text{H}_2\text{S}$ , below 1 ppm of halogen (Cl in coal-derived gas tends to be in the 1 to 500 ppm range), and up to 0.5 vol %  $\text{NH}_3$  appear to be acceptable for short times, but an anode with long-term tolerance is needed. Alloying additions and coatings are being investigated. Generic work on particle filters and gas separation materials can contribute to solutions.

Cathode: Nickel powder is compacted or sintered to the desired pore density and distribution, oxidized, and lithiated in situ. Rates of nickel dissolution at the cathode and reprecipitation at the anode increase with increasing pressure and are a major impediment to 10-atm operation; ambient cell operation can be projected to 40,000 h. Reprecipitated nickel alters the porosity and catalytic activity of the anode and causes shorting. Sintering nickel cathodes increases strength, reduces surface area, and changes pore size distributions, with negative net electrical effects. Carbonate doping may reduce dissolution rates. Alternate cathode materials such as Mn-doped  $\text{LiFeO}_2$  are being explored.

Less than 1 ppm  $\text{H}_2\text{S}$  at the cathode can be tolerated at 1 atm for high fuel utilization, and less is tolerated with increasing temperature and pressure; 40,000-h continuous operation may require <0.01 ppm sulfur.

Structural and Sealing Components: Corrosion of the bipolar separator is a particularly difficult problem, since the  $P_{\text{O}_2}$  can be  $10^{-22}$  to  $10^{-24}$  on the anode side and  $10^{-1}$  on the cathode side for long times at 600 to 700°C. High-temperature alloys including austenitic stainless steels, Ni- and Co-base alloys, and Si- or Al-bearing alloys, both exposed and coated have been explored. Internal resistance losses

from corrosion of current collectors, low structural integrity, and electrolyte loss at wet seals can all be corrosion related. Sealing problems of externally manifolded systems depend on whether the matrix extends through the seal (wet seal) or ends internally at a seal gasket. Vapor-deposited alumina selectively deposited at wet seal areas is a current solution that may not be optimum for the long term. The design option of internal manifolding eases the wet sealing problem but exacerbates the matrix integrity problem.

Additional corrosion in this area is anticipated with the introduction of 1 ppm S, a reasonable level for coal-derived fuels.

Carbonate Management: The lack of a non-wetting material at the operating temperature of MCFCs makes carbonate migration from the electrolyte matrix and sealing more difficult than if such a material could be incorporated into the electrodes. Failing in this approach, improved materials to reduce electrolyte movement past the manifold seal areas or cell seal areas are needed.

#### 6.1.4 Solid Oxide Fuel Cells

SOFCS operate by diffusion of either  $H^+$  or  $O^-$  through a solid electrolyte layer to provide charge transport; most current development work is on oxygen-transporting materials. There are several cell design concepts under active development: planar, tubular, and monolithic (stacked, corrugated planar devices). The Westinghouse tubular design is nearest commercialization. Only one practical materials system, based on yttria-stabilized zirconia (YSZ) electrolyte, has been demonstrated; exploratory work may yield others. Achieving high overall system efficiencies at the operating temperatures of current SOFCs requires bottoming cycles for waste heat recovery. Cell voltages and efficiencies should benefit from high pressure or high oxygen potential at the cathode, but the relatively fragile construction of SOFCs has discouraged pressurization by most developers. Monolithic SOFCs have high projected power densities ( $4000 \text{ kW/m}^3$ ) and specific powers ( $8 \text{ kW/kg}$ ), compared to other state-of-the-art fuel cells ( $140 \text{ kW/m}^3$  and  $0.097 \text{ kW/kg}$ , respectively). Generic solid state electrochemical research in this area is highly appropriate

to the AR&TD Materials Program, since cells driven in reverse can be versatile chemical separation devices.

Materials issues fall into two general categories that are inextricably connected: basic materials selection issues affecting electrical properties and cell lifetime, and the matching of materials characteristics to manufacturing processes. Any program must address both sets of issues to be practical. The discussion is broken into near-term efforts to use the YSZ system (or some modification thereof), and longer-term efforts to find an alternative system.

Fuel Preparation: At 1000°C, the operating temperature of a YSZ SOFC, practically all light hydrocarbon fuels dissociate in the presence of inexpensive nickel or cobalt catalysts. If a hydrocarbon fuel is mixed with steam for reforming, a mixture of hydrogen and carbon monoxide can be used as fuel.

Electrolyte: Electrolytes are selected to have high oxide ion or proton diffusivities, but low cation diffusivities and low electronic conduction at the operating temperature, and stability in both oxidizing and reducing conditions. Thin (perhaps 20  $\mu\text{m}$ ) electrolyte layers have low resistivity; they must be dense and free of defects through the thickness over large areas to develop appreciable power at about 1 V and 200 to 400 mA/cm<sup>2</sup>. For most fuels, measures of cell electrical efficiencies decline with increasing temperature.

Yttria-stabilization of zirconia yields good electrical characteristics and suppresses phase transformations that cause discontinuous changes in properties, particularly density, between room temperature and the operating temperature of about 1000°C.

Anodes: Porous precious metals are sometimes used in experimental cells, but most attention is currently focused on porous cermet catalyst support and current-conductor materials. Metallic nickel or cobalt supported on yttria-stabilized zirconia are currently popular choices for the YSZ electrolyte. This selection does minimize fabrication path and shrinkage, as well as thermal expansion and thermal cycling mismatch difficulties.

Cathodes: Porous precious metal cathodes are sometimes used in modeling work, but porous semiconducting ceramics are more likely for

commercial service. Strontium-doped lanthanum manganite perovskite  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $0 < x < 0.05$ ) and  $\text{La}_{1-y}\text{CaMnO}_3$  ( $0 < y < 0.6$ ), p-type semiconductors, are reasonably compatible with the electrolyte both chemically and physically.

Interconnects: Electrical current conductors (interconnects) must function over a wide range of oxygen potentials without reacting with any other system components to form electrically resistive phases or interfaces. The common choice is magnesium- or strontium-doped lanthanum chromite.

Westinghouse Tubular Construction: Cells are built on 12- to 13-mm-OD porous calcia-stabilized zirconia support tubes. Modified lanthanum manganite is slurried over the tubes and fired at 1400 to 1500°C to form a 0.07-cm-thick porous cathode. Electrolyte material is electrochemically vapor deposited (EVD) from 1200 to 1400°C zinc chloride vapor to a typical thickness of 0.004 cm. Interconnection material, 0.004 cm of magnesium-doped lanthanum chromite, is also deposited by EVD. A 0.001-cm-thick slurry-coated nickel-zirconia or cobalt-zirconia cermet anode is fired below 1000°C. Interconnects are nickel-plated and the cells are connected with a nickel felt.

Materials problems associated with this concept include:

(a) The calcia-doped zirconia support tube destabilizes slowly above 1000°C during later manufacturing processes. A thermodynamically stable, thinner support tube would be an advantage.

(b) The EVD process that allows deposition of electrolyte and interconnect material without oversintering the already-deposited electrode materials is very expensive and cannot by itself deposit certain electrode compositions of interest.

(c) Electrically insulating phases can form at the cathode-electrolyte interface. About half of the total cell infrared loss is in the cathode, making a lower resistivity material desirable. A thicker, self-supporting cathode might eliminate the support tube. A doped lanthanum manganite with more tolerance to reducing conditions is desired. Exposure to fuel during upset conditions causes dimensional changes and cracking as oxygen is exchanged.

(d) Diffusion of dopants from electrodes into the electrolyte during fabrication and operation can significantly change the properties of the electrolyte.

(e) Defects in the electrolyte can cause hot spots in the fuel cell, and both prevention and detection of defects should be upgraded.

(f) Relatively high current densities in the anode near the interconnect can cause voltage-driven interdiffusion and hot spots.

(g) The interconnect material undergoes a phase transformation at 300°C. Calcium or strontium doping would be an improvement, but it is not compatible with the current manufacturing process. Any process requiring sintering of lanthanum chromite is not compatible with the rest of the process, since it sinters at about 1700°C.

Monolithic SOFC Construction: Garrett AiResearch, Combustion Engineering, and the Argonne National Laboratory are a consortium pursuing a cofired monolithic construction featuring a corrugated anode-electrolyte-cathode honeycomb sandwich that resembles cardboard, with the corrugations serving as fuel and oxidant channels. The ceramic tape casting technology used is common in the electronics industry; there are several approaches to forming and bonding the layers. The electrolyte and electrode chemical compositions are similar to Westinghouse's system, but they are laid up simultaneously with different green densities designed to shrink at the same rates during binder burn-off and firing, without cracking or significant distortion. Important concerns are:

(a) Ceramic formulation shrinkages must match during binder removal and firing to avoid warpage and cracking.

(b) The thermal expansion coefficients of the individual components of a cell must match closely to avoid fracturing during thermal cycling.

(c) Process and material control and reproducibility of extraordinary quality will be required. A single defect can cause rejection of a large fuel cell element.

(d) Locally high current densities occur where the interconnect and the electrodes contact.

(e) The electrode-electrolyte composites pose delamination problems.

(f) The strength and fracture toughness of the electrolyte should be improved.

(g) The anode is not perfectly matched in thermal expansion with the rest of the system, and should be more compliant.

(i) A sinterable interconnect is needed.

Flat Plate Construction: International Fuel Cells (IFC) and Ceramtec are pursuing a flat plate design in which the flat anode-electrolyte-cathode layer will be separated by a crossflow bipolar plate that provides structural support and controls gas flow. A flat, impermeable 0.051- to 0.127-mm-thick (0.002- to 0.005-in.) electrolyte accepts screen printed electrodes; plasma spraying has also been used.

Additionally, Z-tek has developed a 1-kW module based on a flat plate proprietary design featuring 10.2-cm-diam (4-in.), 0.25-mm-thick (0.010-in.) flat, stackable electrolyte layers. Their materials are not necessarily those of the Westinghouse system. Flat plate systems are not sufficiently defined to develop independent comments.

Advanced materials work ranges from doping studies through attempts to use design or process technology to avoid or minimize the effects of known difficulties. A major breakthrough may result in an improved SOFC.

Stabilization of the cubic form of zirconia has been achieved by doping with calcia, yttria, ytterbia, heavy rare earth oxides from dysprosia to lutetia, and scandia. There exists a possibility that some dopant or combination of dopants not yet discovered may produce a more useful zirconia-based system.

Ceria ( $\text{CeO}_2$ ), thoria ( $\text{ThO}_2$ ), and yttria have lower ionic conductivity than zirconia. Ceria develops electronic conduction under reducing conditions. Doped bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) conducts as well at 850°C as zirconia does at 1000°C but is unstable under reducing conditions on the anode side. Yet the electrical efficiency gain from operating at lower temperature leads to persistent interest in  $\text{Bi}_2\text{O}_3$ ,

Perovskite oxides, bismuth trioxide-doped zirconia, bismuth trioxide-doped tungsten trioxide, layered structures such as  $K_{0.72}(In_{0.72}Sn_{0.28})_2$ , alkali metal aluminates, and certain superionic conduction oxides.

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## 7. COAL PREPARATION AND HOT-GAS CLEANING

### 7.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

The combustion of coal represents a large portion of the electrical energy generation capability in the United States, and with increased attention to environmental effects and economics, efficient and effective coal cleaning techniques are assuming a more important national role.

Acid rain, resulting in part from the combustion of high-sulfur coals, demands an immediate solution to mitigate irreversible effects on our ecosystem. Flue-gas cleaning systems are expensive and fail to remove all the sulfur from the coal combustion products. Proper coal cleaning is a more attractive alternative, although typically the bound sulfur is difficult to remove. In addition, the performance and efficiency of coal combustion facilities are dependent on the quality of the input coal. Evidence of inorganic mineral matter in the feed coal, which transforms and reacts during the combustion process, can be found in both the coal slag and fly ash waste products. Slag and fly ash have highly deleterious erosive and corrosive effects on the components of combustion facilities, leading to expensive rebuilding and loss of power generation availability. Attention is being directed today toward the development of coal-liquid slurries as fuels for conventional combustors and in direct coal-fired turbines and diesels. For these advanced processes, it is especially critical that highly cleaned coals be used.

#### 7.1.1 Coal Cleaning Processes

The principal objective of any coal preparation process is to remove the mineral impurities, including organic and inorganic sulfur compounds, to levels acceptable for the environmentally safe and economical combustion of the coal. Coal preparation techniques are generally classified as either physical coal cleaning or chemical coal cleaning. Physical cleaning of coal extracts only the coarser forms of mineral matter, including pyritic sulfur, leaving the organic sulfur

compounds intact. To reduce the organic sulfur and, thereby, the total sulfur content of the coal below the levels possible with physical coal cleaning, chemical cleaning is used. Chemical cleaning methods, in conjunction with physical cleaning, have demonstrated the ability to remove greater than 90% of the total sulfur from some coal. In addition, an acid wash can remove 95 to 98% of the ash in the coal.<sup>1</sup>

Gravity separation processes separate coal impurities by specific gravity. These processes typically use mechanical separators such as sifting tables and cyclones to separate the mineral matter. Other processes, such as froth flotation, separate impurities on the basis of differences in the surface properties of the coal and the mineral matter. Materials problems encountered with gravity separation processes are primarily erosion of pipes, chutes, cyclones, and screens. The problems of erosion and wear in physical coal preparation systems are more serious with high-ash coals. A high-ash coal, containing significant amounts of hard minerals (e.g., quartz and chert) and other inorganic matter is much more erosive than a low-ash coal. Pipe erosion occurs primarily at elbow locations, and often the simplest approach to eliminating the problem is to redesign the eroded area. For example, the eroded elbow is removed, and the area redesigned to include a blind tee. The blind tee initially catches the solids, and the collected solids then become the impingement surface, preventing further erosion and eventual failure. Chute wear is minimized through the use of hardened steel surfaces. Protective coatings, including plasma-sprayed coatings, are candidates for the critical surfaces of gravity separation cyclones to reduce wear in these devices. Screen wear occurs at the site of impingement, and operators minimize this problem by periodically rotating the screens. Rubber coating reduces screen wear, but this solution is expensive and reduces the capacity of the screens.<sup>1,2</sup>

Although very effective in the removal of sulfur compounds and ash, chemical cleaning methods introduce corrosive fluids at high temperatures and pressures. As an example, the Ledgemont Oxygen Leaching Process is based on the aqueous oxidation of the pyritic sulfur in coal at elevated temperatures and pressures, in a stream of oxygen. The process is capable of removing more than 90% of the

pyritic sulfur in coals of widely differing ranks. The principal problem with the process is associated with the presence of high-temperature (120°C) dilute sulfuric acid at pressures up to 15 atm. At these temperatures, the dilute acid is highly corrosive and a suitable protective lining is needed for all pieces of equipment exposed to the acid. A 60Ta-40Nb alloy has been suggested, but the cost of using this material would make the process uneconomical.<sup>1</sup>

Another example is the Battelle Hydrothermal Coal Process, which is based on the hydrothermal alkali leaching of mineral and organic sulfur compounds from coal. Severe corrosion problems occur in the desulfurization reaction, since alkalis at temperatures of 250°C in the presence of water are capable of initiating stress corrosion failures of materials. The only material that has been demonstrated to withstand the alkali attack is Inconel 671; however, this material has never been tested in actual operating conditions. In addition, it is expected that the Inconel 671 would be prohibitively expensive.<sup>1</sup> The Jet Propulsion Laboratory process uses chlorine, hydrogen chloride gas, hydrochloric acid, and dilute and concentrated sulfuric acid. The materials needed to overcome problems of corrosion in this process will be very expensive.<sup>1</sup>

Advanced cleaning techniques can produce ultrafine pulverized coals with less than 1% ash for the manufacture of coal-liquid slurries. The principal materials problems with the production and use of coal-liquid slurries arise from the caustic nature of the chemicals that must be added to the slurries to impede agglomeration. In addition, the residual ash and mineral matter in the coal stock cause wear and erosion problems. Corrosion, erosion, and wear of slurry mixers, pumps, transport pipes, and feed systems, either in the production process or in the transport system to the combustor, present significant materials problems. The corrosive and erosive nature of the ash particles and mineral matter in the slurry is accelerated by degradation processes of the slurry, such as changes in viscosity, pH, and particle size.<sup>2</sup> The production of ultraclean coals for direct coal-fired turbines and diesel engines is necessary to minimize wear of turbine blades. Coatings can reduce some of the wear, but long-term operation will ultimately depend on the quality of the feed coal.

Materials problems in coal preparation are largely due to corrosion, erosion, and wear. Projects on the AR&TD Materials Program which address such problems are discussed in Part III. The results from current and past AR&TD Materials Program research on problems of erosion and corrosion in coal liquefaction, gasification, and combustion environments contribute to the understanding of erosion problems in coal preparation schemes.

#### 7.1.2 Hot-Gas Cleanup/Particulate Filters

Several advanced coal technologies will benefit significantly from the development of hot-gas cleanup technology. Several techniques have been considered for the removal of particulates from hot-gas streams, including ceramic bag filters, ceramic crossflow filters, particle bed filters, and ceramic candle filters.

In addition to problems with durability and cleanability, early versions of ceramic bag filters did not have adequate filterability because of large pores within the layers of cloth. Seamless bags offer improvements, but problems with adapting bag clamps and screen supports to hot-gas conditions remain. Crossflow filters are very efficient in removing particulates, but require complex construction. Particle bed filters do not offer the needed efficiency.

Ceramic candle filters are promising candidates, provided they are sufficiently strong and tough and are made from corrosion-resistant materials. Monolithic ceramic candle filters are available commercially and have been used in gasification pilot plants both in the United States and abroad. These filters are generally good in regard to their filtration efficiency, but they fail due to thermomechanical stresses and chemical attack (such as alkali) of the binder phase of the ceramic. In operating pilot plants, process upsets have resulted in stresses on the candle filters sufficient to cause failures. Also, candle filters are subject to failure at the flange/candle body interface, but this problem can be mitigated with rounded flanges. Clearly, a need exists to develop a properly designed ceramic filter that can not only withstand the high-temperature environments, but which can also tolerate changes in system operations that result in severe thermal and mechanical shock.

The AR&TD Materials Program has developed materials with improved properties for use in fossil energy systems. One material developed is a ceramic fiber-ceramic matrix composite made by chemical vapor deposition (CVD). In this process, a reactive gas [methyltrichlorosilane ( $\text{CH}_3\text{Cl}_3\text{Si}$ )] which decomposes at high temperature ( $1200^\circ\text{C}$ ) is forced through a fibrous preform. Silicon carbide is thus deposited on the fibers, bonding them together, and partially filling the space between fibers. Ceramic fiber-ceramic matrix composites with fiber volumes of up to 60% and about 90% of theoretical density have been made. Because of the fiber reinforcement, such composites have shown exceptional strain tolerance, thus overcoming the problem of brittle fracture which limits the performance of most ceramics.

In related work sponsored by the DOE Morgantown Energy Technology Center, the chemical vapor infiltration (CVI) process has been modified to produce ceramic fiber filter materials for use in hot-gas cleanup systems. Fibrous preforms containing fibers of the appropriate diameter, length-to-diameter ratio, and volume loading are being infiltrated with a ceramic matrix to provide the required strength and toughness, and sufficient porosity to provide adequate gas flow through the porous fiber medium. Such a composite has been shown to provide excellent filterability and clean-ability and should have the mechanical properties required to tolerate the cyclic stresses imposed on ceramic filters. In addition, since these materials do not have a binder phase, the potential problem of chemical degradation should be obviated.

Additional development work is needed to scale up the CVD process to produce full-size candle filters and to test them in realistic environments typical of coal combustion and gasification. Ceramic compositions which are not affected by alkali compounds and steam are needed. Protective coatings may also be used to minimize the effects of the process environments. The effects of ash, particularly molten ash, on ceramic filters should also be investigated. Different binders and different fabrication techniques may also be useful in improving the durability of the filters and their resistance to the environments.

## 7.2 REFERENCES

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## 8. TECHNOLOGY DEVELOPMENT AND TRANSFER

### 8.1 TECHNICAL ASSESSMENTS

One of the more important responsibilities of the AR&TD Materials Program is responding to technical issues and research and development needs of both established and emerging fossil energy systems. The assessment of materials problems and needed research to solve those problems in a wide variety of fossil energy technologies is the foundation of an active and relevant research program. The AR&TD Materials Program fulfills this responsibility through technical assessments of materials needs in fossil energy systems.

Several assessments have been performed as a part of this program. In FY 1980, an assessment of materials research needs for fossil energy was performed.<sup>1</sup> This assessment was fairly comprehensive and provided background information relative to the various fossil energy technologies. The aim of the assessment was to identify materials research and development which, if successful, would improve the viability and economics of fossil energy processes. The assessment was presented by materials-related disciplines including the design-materials interface, materials fabrication technology, corrosion and materials compatibility, wear phenomena, ceramic materials, and nondestructive testing. The needs of these various disciplines were correlated with the emerging fossil energy technologies that require materials considerations. Much of the needed research identified in that assessment has been implemented and, in some instances, completed. \*

An assessment was completed in late FY 1982 to identify and quantify the critical (strategic) materials requirements for a generic coal liquefaction facility.<sup>2</sup> It was performed as an engineering estimate of materials requirements based on engineering and technical data for this type of synthetic fuel facility.

An assessment completed in FY 1985 determined the status of materials technology for advanced coal-fired power systems and identified materials research and development that would permit the design,

construction, and reliable operation of more efficient power plants.<sup>3</sup> To establish performance criteria for materials, a pulverized-coal power plant employing an advanced steam cycle with improved efficiency was defined. Materials R&D needs and areas of research that will provide the greatest return in terms of improved efficiency and plant availability were identified. The assessment identified materials for superheaters and reheaters as the development that could have the greatest technical and economic impacts on these systems. Work was initiated on the development of advanced austenitic steels that would have the required properties to meet the performance criteria. This work should be completed in FY 1990 or 1991 and should provide alloys with properties far superior to those of conventional austenitic stainless steels.

Acurex Corporation recently completed an assessment of the causes of failure of ceramic filters for hot-gas cleanup in fossil energy systems.<sup>4</sup> This report identified the critical problems associated with the use of ceramic filters and identified needed research and development to assure that the potential of these ceramic filters is realized. Work has been initiated at the 3M Company to develop a new type of ceramic candle filter using a ceramic fiber-ceramic matrix structure. This development will, if successful, provide a ceramic filter that can withstand the thermal and mechanical stresses of hot-gas cleanup systems as well as withstand the deleterious effects of the harsh process environments.

The Babcock and Wilcox Company, with support from Solar Turbines, Inc., has recently completed an assessment of the potential applications of structural ceramic composites in gas turbines.<sup>5</sup> The most promising applications identified for ceramic composites in gas turbines were the airfoil-shaped nozzle vanes and rotor blades in the turbine hot end. The application of ceramics to these components offers large potential increases in system performance. Combustor liners or turbine inlet ducting components were also identified as potential components for ceramic composites, but little benefit would be obtained by their use. As a result of this assessment, future research and development needs were identified to use ceramic

composites in coal-fired gas turbines. These needs are being incorporated into our planning of projects for future years.

Technical assessments of the fossil energy technologies such as those described above are conducted on a continuing basis to determine research projects which should be initiated on the AR&TD Materials Program. Projects initiated will be required to meet the criteria of generic or crosscutting research of a fundamental or exploratory nature.

## 8.2 TECHNOLOGY TRANSFER

Technology transfer is achieved on the AR&TD Materials Program by several techniques including dissemination of information, cost-shared projects with industry, and formation of consortia to fund projects with the express intent of transferring developments on the program to the industrial sector.

In regard to the dissemination of information, a bimonthly newsletter, *Materials and Components in Fossil Energy Applications*, is published.<sup>6</sup> This document provides for the collection, evaluation, and dissemination of information pertinent to the use of materials and components in fossil energy systems. This project, conducted by Battelle Columbus Laboratories under subcontract, has been a very effective means of information and technology transfer.

Progress reports for the program are published semiannually and include contributions from all participants on the program.<sup>7</sup> This series of progress reports was initiated in FY 1981 and has been extremely useful in providing information to the fossil energy community in a timely fashion. In addition to progress reports, topical reports and open literature publications as well as presentations at technical society meetings are used to transfer information about activities on the program. Another program publication is a bibliography of publications by both past and current participants on the program.<sup>8,9</sup> A conference on Fossil Energy Materials is held annually to present research results of all projects on the program. These reports

and meetings represent a very comprehensive information transfer activity.

Technology transfer is most often achieved through cost-shared projects with industry. For example, a project to use an ORNL-developed technique for producing ceramic fiber-ceramic matrix hot-gas cleanup filters was recently initiated at the 3M Company. This project will result in the fabrication and testing of several full-size candle filters and, more importantly, the establishment of an industrial capability for producing the filters.

One of the most exciting materials developments on the Program is a ductile iron-aluminide alloy. This alloy has very good high-temperature (up to 600°C) strength and outstanding corrosion resistance. The sulfidation resistance of this alloy is superior to that of any commercial or developmental alloys being considered as structural materials in coal gasification plants. To assure the early use of this alloy in an industrial application, ORNL is working with Ametek Specialty Metals Division, Pall Corporation, and the DOE Morgantown Energy Technology Center to produce sintered porous metal filters made from one version of the alloy. In this effort, ORNL will provide material specifications to Ametek. Ametek will produce powder and provide it to Pall Corporation, the filter manufacturer. Pall will fabricate several filters, and the filters will be tested at Morgantown. Pre- and post-test evaluations will be performed by ORNL.

Another approach to technology transfer that is being used is the formation of consortia with industrial organizations to extend developments on the Program to the point that commercialization by industry is assured. A pioneering effort of this type was made in FY 1988 by the establishment of a consortium of ORNL and 12 industrial firms to develop a user-friendly and intelligent software system for the thermomechanical stress analysis of refractory systems. This software incorporates a finite element analysis model developed at Massachusetts Institute of Technology under AR&TD Materials Program subcontract. The MIT model, as developed, is extremely useful in the design of refractory systems, but it is somewhat complex and requires expertise not generally available in many industrial organizations.

The user-friendly and intelligent software being developed will permit the use of this very powerful design tool by engineers not necessarily expert in either finite element analysis or refractory design.

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PART III

CURRENT AND PLANNED PROJECTS OF  
THE FOSSIL ENERGY AR&TD MATERIALS PROGRAM



## 1. CERAMICS

### 1.1 RESEARCH OBJECTIVES

One goal of this research is to understand the relationships between the chemical composition, microstructure, and properties of structural ceramic composites. This understanding should lead to improvements in toughness, corrosion resistance, and resistance to fracture in these ceramic materials. Another objective is to develop ceramic composites for structural applications and use as filters in gas cleanup. Underlining these goals is desire to produce more efficient and lower cost fossil energy systems.

An important facet of this program element deals with the ceramic fiber-ceramic matrix composites produced by chemical vapor infiltration (CVI). In these studies, the interfacial bonding between fiber and matrix is crucial and is receiving considerable attention. Significant investigations are also included that deal with the mechanical properties, performance, and reliability of advanced ceramic composites. Another study is concerned with the joining of fiber-reinforced ceramics. Others deal with the development of new technology materials such as solid state electrolyte systems materials, catalyst support materials; and ceramic membranes for new, high performance fossil systems. Projects involving the nondestructive testing of structural ceramics and microwave sintering of fuel cell materials are also included in the program.

Current and planned research projects in this program element are described in the following section and are listed in Table III.1 at the end of the section.

## 1.2 SUMMARIES OF CURRENT AND PLANNED RESEARCH

### 1.2.1 Structural Ceramic Composites

1.2.1.1 ORNL-1(A). "Fabrication of Ceramic Fiber-Ceramic Matrix Composites by Chemical Vapor Infiltration," Oak Ridge National Laboratory. The purpose of this task is to develop a ceramic composite having higher than normal strength and toughness yet retaining the normal ceramic attributes of refractoriness and high resistance to abrasion and corrosion. This will be accomplished by forming the matrix using a comparatively low-stress, low-temperature process that will avoid the pitfalls of conventional ceramic processing. The technical approach includes eight tasks: (1) parametric examination of infiltration conditions; (2) development of improved fibrous preforms; (3) infiltration of improved preforms with SiC; (4) preparation of composites using overcoated fibers; (5) preparation of composites using alternate fiber types; (6) development of improved matrix materials; (7) infiltration of optimized preforms with improved matrices; and (8) characterization of composites and correlation of process variables, microstructure, and properties. Others have used CVI for fabricating ceramic composites; it has been used to prepare fiber composites with matrices of carbon and/or ceramics such as SiC, Si<sub>3</sub>N<sub>4</sub>, B<sub>4</sub>C, BN, and TiB<sub>2</sub>. Because of their promising mechanical properties, fiber-reinforced composites with SiC and Si<sub>3</sub>N<sub>4</sub> matrices are being fabricated. Computerized equipment will, at first, be used to monitor the experimental variables of the CVI process and later to control the process conditions. Process models being developed at Georgia Tech Research Institute and elsewhere will be tested and evaluated with the goal of improving the microstructure and properties of the composites. The mechanical properties of the composites with various fiber types (e.g., Nextel, Al<sub>2</sub>O<sub>3</sub>, improved SiC fibers, etc.) and matrices (Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) will be determined and compared with previous composites so that the optimum fiber and matrix types can be selected. Future plans include the building of equipment (15-cm-diam furnace) that can be used

to fabricate larger engineering-scale specimens and emphasis on oxide matrix composites for oxidation and/or corrosion resistance.

1.2.1.2 ORNL-1(C), "Characterization of Fiber-CVD Matrix Interfacial Bonds," Oak Ridge National Laboratory. The purpose of this task is to optimize the strength and toughness of fiber-reinforced ceramic composites by controlling the bonding and frictional stresses at the fiber-matrix interface. Composites with both high strength and adequate fracture toughness can only be obtained by transferring the load to the fiber while exhibiting significant fiber pullout. Pyrolytic carbon coating of Nicalon fibers by Amercom and Refractory Composites resulted in improvements in mechanical properties in SiC matrices. The strength of the interfacial bond between the SiC matrix and the Nicalon fiber was reduced, which resulted in increased fiber pullout and improved fracture toughness. The effect of controlling interfacial bond strengths will be further investigated so that fiber pretreatments or coating processes can be developed which optimize the strength and fracture toughness of various composite systems. The goal of this project is to demonstrate that the interfacial bond between Nicalon fibers and various ceramic matrices can be measured and controlled for optimization of mechanical properties such as strength and toughness. The technical approach for this project includes four tasks: (1) develop interface characterization techniques, (2) develop bond strength measurement techniques, (3) determine candidate overcoat compositions and develop overcoating of fibers, and (4) characterize composites and correlate fiber-matrix bonding with strength and strain tolerance. The mechanical properties of optimized composites, including room-temperature strength, high-temperature strength, and fracture toughness, will be determined and correlated with the fiber-matrix bond strengths. Additional studies will continue to focus on the stability of the composites and interlayers at elevated temperature in oxidizing or corrosive environments.

1.2.1.3 GT-1, "Development of Advanced Fiber-Reinforced Ceramics," Georgia Tech Research Institute. The objective of the program is to develop an understanding of the critical factors in composite processing and to use this improved understanding to develop a silicon nitride composite microstructure for increased fracture toughness. The critical factors to be addressed are the nitriding process, the fiber-matrix interface, and processing-induced fiber orientation and residual porosity. X-ray diffraction (XRD), Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), secondary ion mass spectroscopy (SIMS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) will be used to characterize the interface region for the whisker- and fiber-toughened silicon nitride materials. This, along with mechanical property evaluation, will allow development of optimized processing conditions. In order to optimize the nitriding process for reaction sintered silicon nitride composites, a computer-controlled nitriding system is being developed. The system will utilize intelligent, real-time control of processing variables to assure complete conversion of the matrix material while minimizing fiber degradation.

1.2.1.4 GT-1(A), "Modeling of Fibrous Preforms for CVD Infiltration," Georgia Tech Research Institute. The purpose of this research is to develop models of various fibrous preforms for CVI processes. The CVI technique has demonstrated considerable promise for fabrication of fiber-reinforced ceramic composites. Unidirectional and bidirectional composites of SiC fibers in a SiC matrix have shown good strength and exceptional strain tolerance. An analytical model provides insight into the CVI process, helps identify key processing parameters, and guides experimental process optimization efforts. The one-dimensional model developed for a random fiber preform has been modified to simulate the densification process with a cloth lay-up preform. A three-dimensional model for the forced CVI process has been developed, although implementation is not complete. Additional experimental measurements are required to provide physical properties and boundary values. Given these, the model will simulate the infiltration process

for a variety of shapes and furnace configurations and assist in development of optimum process conditions.

1.2.1.5 LANL-1, "Vapor-Liquid-Solid SiC Whisker Process Development," Los Alamos National Laboratory. This program addresses the need to improve the fracture toughness of whisker-reinforced ceramics to achieve both high and reliable strength characteristics, and non-catastrophic failure. The latter implies the existence of residual load-carrying capability after initial failure. Our approach is to extend the vapor-liquid-solid (VLS) process used to grow short SiC whiskers to the growth of long whiskers (up to 100 mm) and develop the use of these whiskers as semi-continuous, oriented reinforcement for ceramic matrices. Two principal tasks are included in this work. One is to modify and optimize the existing VLS whisker growth process to produce long SiC whiskers. As part of this task, the groundwork will be established to incorporate an artificial intelligence (AI) system in the whisker growth process. An AI system offers the potential for markedly improving the yield, quality, and reproducibility of a product at a fraction of the human resources. Such a payoff is especially attractive from the standpoint of technology transfer. The use of the long whiskers will require some reassessment and modification of the harvesting and beneficiation procedures used for short whiskers. The second task entails the development of a staple whisker yarn. To help predict the performance of the yarn in composites, work will continue in characterizing the strength of long VLS SiC whiskers as a function of temperature and surface treatment. A portion of this research is supported by Los Alamos National Laboratory General Materials and Process Development funding and the DARPA/Los Alamos IMA Program.

1.2.1.6 INEL-1(A), "Nondestructive Evaluation of Advanced Ceramic Composite Materials," Idaho National Engineering Laboratory. The objective of this program is to evaluate and develop nondestructive evaluation (NDE) techniques for advanced ceramic composite materials. The capabilities of state-of-the-art NDE techniques to reliably

detect and characterize defects will be determined. New and/or improved techniques will be developed as the needs are identified. A SiC-reinforced SiC matrix composite is the first material system being studied. The material is fabricated by infiltrating fibrous preform structures with vapors that deposit on the fiber surfaces to form the matrix of the composite. Techniques to detect and characterize porosity and individual voids, known to be produced in the material and decrease its strength, are being investigated first. A physical and mathematical model of the propagation of ultrasound through the ceramic composite is being developed that should help relate ultrasonic measurements to sample porosity, help predict the detection limits for voids, and provide guidance for developing single-sided inspection techniques. To date, the model achieves good qualitative results. Noncontacting laser vibration detection methods and acoustic emission measurements will be used to study the fiber-matrix interface.

1.2.1.7 INEL-1(B), "Joining of Silicon Carbide Reinforced Ceramics," Idaho National Engineering Laboratory. This research program will identify and develop techniques for joining SiC-fiber-reinforced ceramic composites of tubular geometries, primarily through the use of glass joining materials. Recently, MgO-Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass with Nb<sub>2</sub>O<sub>5</sub> additions was used to successfully join SiC-fiber-reinforced-SiC matrix composites. The general tasks of this program include identifying, preparing, and characterizing compositions suitable for joining ceramic-ceramic composites; developing a joining methodology and evaluating the effects of process parameters on joint characteristics; fabricating and characterizing joints; and determining physical-mechanical properties and failure behavior of joints under ambient conditions, elevated temperatures, and simulated service environments.

1.2.1.8 VPI-1, "Investigation of Properties and Performance of Ceramic Composite Components," Virginia Polytechnic Institute and State University. The central objectives of the program are to: (a) develop an understanding of the mechanical behavior of advanced composites subjected to elevated temperature and dynamic (cyclic) loading, (b) develop a test system and test methods that will be used to obtain

the properties and performance information required to design engineering components made from ceramic composite materials, and (c) provide critical and comprehensive evaluations of such materials to material synthesizers and developers. Specific objectives include the following:

- (1) A mechanical test device using a servohydraulic test frame designed for multiaxial loading will be designed and constructed.
- (2) The room-temperature response of several material types of ceramic composite tubes to quasistatic-uniaxial loading will be established. The strength, stiffness, and failure modes of those tubes, the statistical variations of those characteristics, and the mechanistic relationship of the microstructure and damage state will be investigated.
- (3) The response of ceramic composite tubes to cyclic loading will be determined.
- (4) The response of ceramic composite tubes under quasistatic- uniaxial and cyclic loads to elevated temperature up to 1370°C (2500°F) will be determined.
- (5) Mechanistic models which are capable of predicting the strength (or residual strength) of ceramic composite tubes subjected to various load histories and temperatures will be developed.
- (6) The need for subsequent work dealing with additional parameters for other component shapes, atmospheres, material systems, load histories, or response characteristics will be determined.

1.2.1.9 NCAT-1, "Mechanical Properties Testing of Ceramic Fiber-Ceramic Matrix Composites," North Carolina A&T State University. The purpose of this effort is to expand the mechanical properties data base for composites fabricated by forced CVI. Composites are currently being fabricated with continuous SiC fiber reinforcement, SiC whisker reinforcement, SiC platelet reinforcement, and continuous aluminosilicate fiber reinforcement. The mechanical properties vary with the type of reinforcement and with the type of coating utilized to control the fiber-matrix interfacial bond. The effect of the reinforcement type and interfacial bond on the tensile strength,

thermal shock resistance, oxidation resistance, and tensile strength during cyclic loading will be investigated.

1.2.1.10 NIST-1, "Structural Reliability and Damage Tolerance of Ceramic Composites for High-Temperature Applications," National Institute of Standards and Technology. With an objective of improved performance for heat engine and heat recovery applications, the NIST program addresses the problems of improved reliability and extended lifetime through determination and characterization of major toughening mechanisms in ceramic composites, examining both model crack-fiber systems and actual composites. A key aspect of the program is determination of the critical processing factors which influence microstructure and interfacial behavior in these materials.

1.2.1.11 ANL-1, "Development of Nondestructive Evaluation Methods for Structural Ceramics," Argonne National Laboratory. The purpose of Part A of this work is to (1) evaluate and develop acoustic, radiographic, and nuclear magnetic resonance (NMR) techniques for NDE of structural ceramics, with emphasis on characterization of formed (green-state) ceramic bodies to obtain information relevant to process control; (2) establish the types of characteristics (density gradients, organic binder/plasticizer distributions, inclusion distributions, etc.) that can be detected by NDE techniques; and (3) determine correlations between the presence of flaws, NDE results, and fracture behavior of densified ceramics in Part B. NDE techniques are being developed to detect porosity, cracking (surface and internal), inclusions, density variations, and binder-plasticizer distributions. The work encompasses monolithic ceramics and ceramic-ceramic composites. Part B of this task is the characterization of the fracture behavior of structural ceramics ( $\text{Si}_3\text{N}_4$ ) with well-defined flaws. Specimens of  $\text{Si}_3\text{N}_4$  with controlled flaws will be fabricated by introducing controlled amounts of pore formers and second-phase additions, such as Fe, Si, WC, and TiC. Selected NDE methods will be used to locate the flaws, and fracture bars will be cut accordingly. The fracture stress, fracture toughness, and elastic modulus of these specimens will be evaluated to establish the effects of microstructural

flaws on the fracture behavior of these structural ceramics. The findings will be correlated with the data from Part A to allow the NDE inspection methods to be quantified.

### 1.2.2 Solid State Electrolyte Systems

1.2.2.1 ORNL-1(D), "Microwave Sintering of Ceramics," Oak Ridge National Laboratory. The purpose of this research is to explore the feasibility of using microwave heating as a means of fabricating electrode and electrolyte materials having improved electrical properties for solid oxide fuel cells. The ultimate goal is to develop the technology for fabricating a complete monolithic fuel cell module in one operation. Two classes of ceramics will be included in this study: (1) cubic  $Y_2O_3$ -stabilized zirconia, the solid electrolyte; and (2)  $La(M^{+2})CrO_3$  type materials, the current interconnectors. The objective for both materials is to produce ceramic bodies having electrical properties superior to those attainable using resistance heating. Since both materials respond differently to the microwaves, it is necessary to understand their individual behavior before they can be fired together. In addition to material composition, variables to be examined include powder processing, green-body fabrication techniques, microwave furnace atmosphere, and heating parameters. The sintered material will be characterized to determine its sintered density, its grain size and uniformity, and, finally, its mechanical and electrical properties.

1.2.2.2 PNL-1, "Advanced Materials/Electrochemical Processes of Solid Electrolytes," Pacific Northwest Laboratory. The objective of this work is to identify and develop new, highly-electrically conducting oxide materials as electrodes, electrolytes, and current connections and to develop an understanding of synergistic effects of materials properties, structures and compositions on the electrochemical processes for high-temperature, solid electrolyte, electrochemical cells. The goals are to:

(a) Synthesize new materials; determine electrical transport, thermal and chemical properties; obtain an understanding of the effects of structure, microstructure, phase equilibria, and composition on these

properties; develop advanced oxide systems based on  $[La, Y](M')(Cr, M'')O_3$  interconnections and  $ZrO_2-MO_2-Re_xO_y-Y_2O_3$  and  $ZrO_2(HfO_2)-Re_xO_y-MO_2$  electrodes for easier fabrication of electrolyte cells with improved electrical, thermal, and electrochemical properties.

(b) Determine the electrochemical interactions and processes between solids/solids/fluids, particularly the role of interfaces, in high-temperature, solid electrolyte systems; understand electrochemical processes, kinetics and mechanisms for charge transfer, adsorption and mass transport relating to ion diffusion, materials interaction, and composition change; develop experimental methods, i.e., complex impedance, coupled with conventional electrochemical techniques; and define accelerated testing based on empirical and theoretical electrochemistry.

### 1.2.3 Catalyst Support Materials

#### 1.2.3.1 SNL-1, "Ceramic Catalyst Materials: Hydrous Metal Oxide Ion-Exchange Supports for Direct Coal Liquefaction," Sandia National Laboratories.

The goal of this project is to develop a fundamental understanding of the preparation and properties of a number of unique catalytic support materials. The following areas will be investigated:

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

Catalyst properties for specific applications will be tailored, and will provide a foundation for further catalyst development. The specific materials under study are from a group of hydrous oxide ion-exchange compounds of Ti, Zr, Nb, and Ta developed at Sandia National Laboratories. These compounds have been used to prepare catalysts by a novel synthesis route involving the incorporation of active metals by ion exchange. The use of these compounds as ceramic catalyst supports arises from the unique properties which these systems exhibit:

- (1) ability to incorporate a metal, or mixture of metals, into the materials over a wide concentration range by a simple process;
- (2) high surface area which increases with increasing temperature;
- (3) good chemical stability;
- (4) solution chemistry or more conventional high-temperature reactions which can be used to provide control of the active metal oxidation state;
- (5) acidity and basicity of the substrate

which can be modified by ion exchange; and (6) catalysts which can be prepared on transition metal oxide supports.

#### 1.2.4 Ceramic Membranes

1.2.4.1 ORGDP-1, "Development of Ceramic Membranes for Gas Separation," Oak Ridge Gaseous Diffusion Plant. The objective of this project is to explore the applicability of inorganic membranes to separate gases at high temperatures and/or in hostile process environments encountered in fossil energy conversion processes such as coal gasification. The program will seek to apply porous membrane technology developed for uranium enrichment to the separation of these gases. The program could lead to the development of processes that would improve the economics of fossil energy conversion processes by significantly reducing gas cleanup and separation costs. The overall R&D program consists of the development of membrane separation systems for the recovery of H<sub>2</sub> and the separation of acid gases (H<sub>2</sub>S, CO<sub>2</sub>) from synthesis gas. The work consists of fabricating and physically characterizing the candidate membranes using the specified techniques presently available at the Oak Ridge Gaseous Diffusion Plant. Efforts will be made to transfer the technology to industry. Another part of this program, which is funded from the Gas Stream Cleanup Program, involves the identification of the candidate membrane materials based upon the chemistry of the separations environment evaluation of the separations capability of the fabricated membranes in terms of permeabilities and fluxes of gases assessment of the worldwide R&D activity in this field and reporting on the project.

#### 1.2.5 Ceramic Filters

1.2.5.1 ORNL-1(B), "Ceramic Filter Development," Oak Ridge National Laboratory. This expanded initiative will look at the chemical vapor infiltration process to produce filters other than candle filters, such as crossflow filters, and materials other than SiC. Candle filter development is being pursued as part of a technology transfer effort with the 3M Company (see 4.2.2.1).

### 1.2.6 New Materials Processes

1.2.6.1 INEL-1(C), "Superconducting Film Fabrication Research," Idaho National Engineering Laboratory. This program investigated techniques for fabricating sol-gel derived films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  based superconducting ceramics with the ultimate goal of developing a fabrication technology that can produce useful devices. One of the first tasks was to develop method(s) of synthesizing alkoxy compounds of copper and yttrium for sol-gel synthesis and fabrication of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconducting films. The general tasks of this program included synthesis of alkoxide precursors; development of sol preparation procedure(s); preparation of sol-gel derived powders; and film fabrication using sol as well as sol-gel superconducting properties, microstructure, and chemical homogeneity. It has already been demonstrated that the sol-gel derived  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductor was more homogeneous than that produced by conventional methods (i.e., solid state reactions of oxides and carbonates).

Table III.1. Research projects for ceramics

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
<b>Structural Ceramic Composites</b>						
ORNL-1(A) - Fabrication of Ceramic Fiber-Ceramic Matrix Composites by Chemical Vapor Infiltration	Oak Ridge National Laboratory (ORNL)	188	245	250	250	250
ORNL-1(C) - Characterization of Fiber-CVD Matrix Interfacial Bonds	ORNL	138	194	200	200	200
GT-1 - Development of Advanced Fiber-Reinforced Ceramics	Georgia Tech Research Institute (GT)	148	150	150	0	0
GT-1(A) - Modeling of Fibrous Preforms for CVD Infiltration	GT	49	50	50	0	0
INEL-1(A) - Nondestructive Evaluation of Advanced Ceramic Composite Materials	INEL	172	175	175	175	175
INEL-1(B) - Joining of Silicon Carbide Ceramic Composites	INEL	173	175	175	175	175
VPI-1 - Investigation of Properties and Performance of Ceramic Composite Components	Virginia Polytechnic Institute and State University (VPI)	a	0	0	0	0

Table III.1. (continued)

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
NCAT-1 - Mechanical Properties Testing of Ceramic Fiber-Ceramic Matrix Composites	North Carolina A&T State University (NCAT)	91	100	100	100	100
NIST-1 - Structural Reliability and Damage Tolerance of Ceramic Composites for High-Temperature Applications	National Institute of Standards and Technology (NIST)	148	150	150	200	200
ANL-1 - Development of Non-destructive Evaluation Techniques and the Effect of Flaws on the Fracture Behavior of Structural Ceramics	Argonne National Laboratory (ANL)	311	350	350	400	400
	<b>Solid State Electrolyte Systems</b>					
PNL-1 - Investigation of Electrochemical Processes in High-Temperature Solid Electrolytes	Pacific Northwest Laboratory (PNL)	296	1000	1000	1000	1000
	<b>Catalyst Support Materials</b>					
SNL-1 - Ceramic Catalyst Materials: Hydrous Metal Oxide Ion-Exchange Supports for Direct Coal Liquefaction	Sandia National Laboratories (SNL)	197	390	390	400	400

Table III.1. (continued)

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
<b>Ceramic Membranes</b>						
ORGDP-1 - Development of Ceramic Membranes for Gas Separation	Oak Ridge Gaseous Diffusion Plant (ORGDP)	327	400	400	500	500
<b>Ceramic Filters</b>						
ORNL-1(B) - Ceramic Filter Development	ORNL	0	190	200	200	200
<b>New Materials Processes</b>						
INEL-1(C) - Sol-Gel Synthesis of Superconducting Ceramics	INEL	<sup>a</sup>	0	0	0	0
LANL-1 - Vapor-Liquid-Solid SiC Whisker Process Development	Los Alamos National Laboratory (LANL)	99	60	60	0	0
ORNL-1(D) - Microwave Sintering of Ceramics	ORNL	197	290	300	300	300
SC-1 - Development of Advanced Materials Processes	To be determine	0	0	0	0	0
TOTALS		2,534	3,919	3,950	4,295	4,205

<sup>a</sup> Refers to carryover funding from previous fiscal year.



## 2. NEW ALLOYS

### 2.1 RESEARCH OBJECTIVES

The objective of the research in this area is to gain a better understanding of the behavior of structural materials used in coal gasification, combustion power, and other fossil systems. This knowledge will enable the continued development of advanced, high-strength materials which range from austenitic stainless steels and other high-temperature alloys to the inexpensive, but highly corrosion-resistant, iron aluminides, and coatings and claddings. These advanced alloys should offer greater service lifetimes and/or lower costs than existing carbon steels and ferritic stainless steels. Work in this area includes mechanical properties, microstructural studies, welding and joining, and corrosion testing. An effort in developing materials processes is proposed for FY 1991 to improve quality, reduce cost, and/or provide the capability to produce new materials and structures.

Summaries of the research and development activities in this program element are described in the following section and in Table III.2 at the end of the section. The research projects are listed under four separate categories: advanced austenitic alloys, iron aluminides, coatings and claddings, and new materials processes.

### 2.2 SUMMARIES OF CURRENT AND PLANNED RESEARCH

#### 2.2.1 Advanced Austenitic Alloys

2.2.1.1 ORNL-2(B). "Development and Evaluation of Advanced Austenitic Alloys." Oak Ridge National Laboratory. The purpose of this task is to evaluate advanced austenitic alloys for the design, construction, and reliable operation of heat recovery systems in coal combustion plants through utilization of higher-temperature advanced steam cycle concepts. The approach is to consult with boiler manufacturers, utilities, and related industrial groups to establish the alloy performance criteria. Factors considered will be strength, ductility, corrosion resistance, stability, fabricability, inspectability, and costs. The availability and performance of existing alloys will then be reviewed

in comparison with the criteria. A program plan has been developed that identifies the needed research to qualify existing alloys, modify existing alloys, or develop new alloys. Concepts in materials science will be used to the fullest extent to select compositions expected to meet the criteria. Industrial subcontractors will supply heats of these alloys, and Oak Ridge National Laboratory (ORNL) and university subcontractors will provide the expertise to screen and evaluate the alloys through experimental work. Exploratory studies of fabrication methods, joining methods, and surface treatments will be undertaken on the most promising alloys. A procedure will be developed whereby the optimum alloy composition and surface treatment can be selected according to the specific performance requirements related to environment, component configuration, fabrication methods, and the load-time-temperature histogram for the component.

2.2.1.2 CU-2, "Mechanical Properties and Microstructural Stability of Advanced Austenitic Alloys," Cornell University. The goals of this project are to (a) obtain mechanical property data which can be used to screen alloys developed for use in advanced steam cycle plants, and to (b) characterize the long-term mechanical properties of the promising alloys. Previous work emphasized correlation of mechanical properties of the 17/14CuMo reference alloy with its microstructural evolution during aging at 800°C for times up to 2146 h. It was concluded that during the initial 200 h of aging there was a 10 to 30% drop in flow strength as a result of coarsening of MC-type precipitates. After the initial drop the flow strength of the alloy was found to level off. This leveling off was consistent with the decreased ripening rate of the MC-type precipitates. The alloys screening portion of the program will be continued using load relaxation tests of advanced austenitic alloys in various states of thermomechanical pretreatment.

2.2.1.3 USC-2, "Microstructural Studies of Advanced Austenitic Steels," University of Southern California. This research aims to (1) characterize the zero stress microstructural evolution during tempering of a type 316 austenitic stainless steel reference alloy, (2) determine the effects of prior deformation (5 to 8% cold work) on

the precipitation kinetics, (3) investigate the influence of copper and phosphorus additions on the kinetics of aging, and (4) compare these data with microstructural observations from stress relaxation and creep-tested specimens. The microstructural studies will provide a data base for phase optimization in these advanced steels. So far, it has been shown that optimization of the mechanical and creep rupture properties of one series of these alloys can be achieved by careful control of solution treatment temperature, stabilizing element additions, and initial dislocation substructure.

2.2.1.4 B&W-2, "Evaluation of the Fabricability of Advanced Austenitic Tubing." Babcock & Wilcox Research. This program addresses the problem of fabricating tubing from alloys containing controlled amounts of minor element additions and cladding or surface treating the tubing for optimum corrosion resistance. The specific alloys have been defined through an alloy screening program that is concerned with strength and metallurgical stability at temperatures in the range of 650 to 760°C. The scope of the program consists of melting experimental alloys, conditioning of ingots and forging of ingots into extrusion billets, and production of seamless tubing. A portion of some of the sample tubing will be clad on the outside with high-chromium, high-nickel alloys (Alloy 671, Alloy 690) for corrosion protection. Specific details on each of the processing routines and results of chemical and metallurgical testing of tubing produced to date are presented in a recent report. Samples of the tubing produced under this task will be used in complementary tasks to examine the mechanical behavior, weldability, and fireside and steamside corrosion of the tubing.

2.2.1.5 UTN-2, "Investigation of Welding and Joining Techniques for Advanced Austenitic Alloys." The University of Tennessee. The objective of this project is to evaluate the weldability of selected austenitic alloys with potential applications in superheaters and reheaters of advanced steam cycles operating at 700°C and 35 MPa pressure. Fabrication procedures, especially by welding, must fall within the realm of standard practice in the fossil energy industry and be consistent with the tenets of the ASME Boiler and Pressure Vessel Code.

The alloys should be free from hot cracking, reheat cracking, heat-affected zone creep rupture property deterioration, and embrittlement in long-time service. It should also be possible to join them with other alloys without long-time interface effects; the filler metals for joining the alloys should be developed concurrently with the alloy selection investigations. Weldability studies have shown that several of the austenitic compositions were marginal for standard fabrication practices and thus a series of alloy modifications were considered based on elevated-temperature properties and weldability. Future work will include restraint hot cracking tests and metallurgical evaluations of the tested samples using analytical electron microscopy.

2.2.1.6 FW-2, "Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coatings, and Claddings," Foster Wheeler Development Corporation. This project consists of three tasks. The first task is a literature search which will provide a review of the literature describing the mechanisms and corrosion data for coal ash corrosion. This review will include published literature; university work; and utility contacts in the United States, and, to a limited extent, in Canada, Great Britain, and Japan. The purpose of the second task will be to generate comprehensive corrosion data for selected superheater and reheater tube alloys in aggressive coal ash environments. ORNL-modified alloys and standard comparison alloys will be tested using a 35 wt %  $\text{Na}_2\text{SO}_4$ , 35 wt %  $\text{K}_2\text{SO}_4$ , and balance  $\text{Fe}_2\text{O}_3$  ash. The exception will be tests of unclad lean stainless steels and modified alloy 800H using a 10% alkali sulfate salt in simulated coal ash. Retort tests will be conducted at 0.25 and 1.0%  $\text{SO}_2$  at 650 and 700°C for 100 and 1000 h. The third task is to evaluate the variables affecting coal ash corrosion and the mechanisms governing oxide breakdown and corrosion penetration. Corrosion rates of the test alloys will be determined as functions of temperature, ash composition, gas composition, and time. A model based on the isocorrosion diagram will be developed to predict corrosion rates for conditions other than the test conditions. Metallurgical analyses, including scanning electron microscopy/energy dispersive X-ray analysis and microprobe examinations, of samples, corrosion

products, and subsurface penetrations will be performed to aid in the understanding of the corrosion process.

2.2.1.7 SC(I,U)-2. "Steamside Corrosion Tests of Advanced Austenitic Alloys," subcontractor to be determined. The purpose of this work will be to investigate the corrosion of the advanced austenitic alloys in steam at 650°C and 34.5 MPa. A two-year subcontract with an industrial firm is anticipated.

## 2.2.2 Iron Aluminides

2.2.2.1 ORNL-2(F). "Development of Iron Aluminides," Oak Ridge National Laboratory. The objective of this task is to develop low-cost, low-density intermetallic alloys based on Fe<sub>3</sub>Al with an optimum combination of strength, ductility, and corrosion resistance for use as components in advanced fossil energy conversion systems. Iron aluminides near the Fe<sub>3</sub>Al composition are expected to be resistant to corrosion and sulfidation in high-temperature fossil energy systems because of their ability to form protective aluminum oxide scales. Until recently, the usefulness of Fe<sub>3</sub>Al has been limited by its low room-temperature ductility (≈1-2%) and poor hot strength above 600°C. Now, with careful alloying and the development of effective thermo-mechanical treatments, a 15% room-temperature ductility and significant increases (as high as 50%) in strength at 600°C have been achieved. Moreover, these improvements have been realized without sacrificing oxidation or corrosion resistance. Future efforts will be aimed at measuring and/or improving other mechanical properties such as creep strength, fatigue strength, and fracture toughness.

2.2.2.2 ORNL-2(A). "Environmental Effects on Iron Aluminides," Oak Ridge National Laboratory. The purpose of this task is to develop protective scales on iron-based alloys in mixed-oxidant (oxygen-sulfur) environments for coal-related applications at 500 to 800°C. Important objectives include (1) development of protective oxide scales by modifying oxide chemistry/microstructure to reduce the transport of sulfur through the scales; (2) formation of a sulfur-diffusional barrier under or above the protective scale to minimize the sulfur

attack; and (3) study of the effects of alloy chemistry, oxide morphology, and temperature on the breakdown of protective scales. Two general approaches are currently being evaluated for achieving sulfidation-resistant scales. One is to establish a thermodynamically stable oxide film on an alloy or coating substrate and the other is to incorporate alloying elements that will form a thermodynamically stable and slowly growing sulfide phase. The first approach uses  $\text{Fe}_3\text{Al}$  as the model system and evaluates the effects of alloying modifications, designed to improve mechanical behavior, on oxidation/sulfidation resistance. The second approach involves the addition of 9 to 18 wt % niobium, a strong sulfide former, to improve the sulfidation resistance of alumina-forming iron-based alloys.

2.2.2.3 INEL-2, "Study of the Influence of Processing on Microstructure and Properties of Aluminides, Idaho National Engineering Laboratory. This program will determine the influence of processing on the properties of alloys based on the intermetallic compound  $\text{Fe}_3\text{Al}$ . Thermomechanical processing of alloys based on  $\text{Fe}_3\text{Al}$  will be pursued to improve the room temperature ductility of these alloys. The response of the microstructure to annealing will be characterized in terms of the establishment of equilibrium phases and equilibrium degree of long range order. The role of dislocation and antiphase boundary structures in enhancing the ductility of  $\text{Fe}_3\text{Al}$  will be investigated. The mechanical properties will be determined at room and elevated temperature and related to the microstructure. Small batches of  $\text{Fe}_3\text{Al}$  powders will be produced by gas atomization at the Idaho National Engineering Laboratory (INEL) for characterization and also consolidation by hot extrusion. The composition of the  $\text{Fe}_3\text{Al}$  alloys and the thermomechanical processing routes will be determined in collaboration with the program at Oak Ridge National Laboratory.

2.2.2.4 CSM-2, "Investigation of the Weldability of Iron Aluminides," Colorado School of Mines and ORNL. This joint investigation was established to study the weldability of polycrystalline  $\text{Fe}_3\text{Al}$ -type alloys, and to correlate weldability to composition, phase equilibria, grain size and morphology, domain size, and degree of long range order. The following specific tasks will be undertaken: (1) select the most

promising composition of Fe<sub>3</sub>Al alloy (with ORNL); (2) apply thermomechanical treatments to create a range of grain sizes in the Fe<sub>3</sub>Al alloy and conduct hot ductility tests, utilizing the 1500 Gleeble (either at GCM or ORNL), to characterize the sensitivity of weldability to grain refinement; (3) use transmission electron microscopy and optical microscopy to characterize the microstructure; (4) use metallography, X-ray techniques, and differential thermal analysis to define the DO<sub>3</sub>/B2 transformation temperature and degree of long-range order; (5) correlate the hot ductility of different test specimens with their respective compositions, domain sizes, and degrees of order; and (6) make electron beam and gas tungsten arc welds that will be evaluated for susceptibility to hot cracking at three widely varying cooling rates.

2.2.2.5 HRWL-2. "Secondary-Ion Mass Spectrometry Study of Scales on Iron Aluminides." Harwell Laboratories. Sheet specimens of Fe-28 at. % Al preoxidized at ORNL, as well as Ni<sub>3</sub>Al reinforced with Al<sub>2</sub>O<sub>3</sub>, will be forwarded to Harwell Laboratories, United Kingdom, for subsequent exposure in oxygen, enriched with <sup>18</sup>O. After exposure, the specimens will be sent to ORNL for metallographic preparation, and then returned to Harwell for secondary-ion mass spectrometry (SIMS) analysis. These analyses will show the location of <sup>18</sup>O and will serve to define the preferred diffusion paths of oxygen in these two materials.

2.2.2.6 SC(I)-2(A). "Evaluation of the Fabricability of Iron Aluminides." subcontractor to be determined. This project addresses the problems associated with fabricating tubing, sheets, and other product forms from iron aluminide alloys. The specific alloys that will be investigated are being identified in project ORNL-2(F), "Development of Iron Aluminides." The scope of the planned project consists of melting experimental alloys, conditioning of ingots and forging of ingots into extrusion billets, and production of seamless tubing. Plate and sheet material will also be produced to further evaluate the fabricability of this material. Samples of the product forms produced on this project will be used in complementary tasks to

examine the mechanical behavior, weldability, and corrosion behavior of the material.

### 2.2.3 Coatings and Claddings

2.2.3.1 OSU-2, "Fundamental Study of Aluminizing and Chromizing Processes," Ohio State University. The purpose of this work is to gain an understanding of the mechanism of simultaneous deposition of chromium and aluminum into iron substrates and to achieve similar diffusion coatings on the surfaces of austenitic and ferritic stainless steels. It is known that the combination of chromium and aluminum in the surfaces of iron-base alloys provides superior resistance to degradation by a variety of high-temperature environments. Pack cementation, which is a modified chemical vapor deposition process, will be employed at an elevated temperature of about 1000°C.. A concurrent computer-assisted thermodynamic study of the equilibrium vapor pressures of volatile species is conducted to aid in the interpretation of the experimental results. A number of different pack alloys are being used to produce chromium-aluminum coatings on such alloys as 2%Cr-1Mo, Fe-12Cr, 304 SS, 316 SS, and Incoloy 800. In the future, decarburization of the surface (to eliminate the initial carbide layer) and the incorporation of reactive elements in the surface (to improve scale adhesion) will be investigated.

2.2.3.2 WHC-2, "Investigation of Electro-Spark Deposited Coatings for Protection of Materials in Sulfidizing Atmospheres," Westinghouse Hanford Company. The objective of this program is to develop candidate coatings, using the electro-spark deposition (ESD) process, for the protection of materials in sulfidizing atmospheres typical of fossil energy applications. Coatings of interest include single or multilayer deposits of commercially available hardfacing alloys, as well as custom formulations of metal aluminides, chromium alloys, refractory metals, carbides, silicides, and borides. Materials to be protected include low alloy steels, Alloy 800, and type 310 stainless steel. ESD coatings of refractory metals also are being developed for use as diffusion barriers between the substrate steel and another corrosion- or erosion-resistant coating. ESD coatings of rhenium on austenitic stainless

steels are completely free of cracking and parameters have been developed that produce an excellent, uniform coating. Experiments are now proceeding with the use of rhenium as an initial layer on 310 stainless steel, with subsequent layers of niobium and other corrosion-resistant alloys.

2.2.3.3 SC(I)-2(C), "Coating and Cladding Process Development," subcontractor to be determined. This project will be concerned with the development of novel coating and cladding processes. The work will include processes for applying iron-aluminide alloys to less corrosion-resistant, but greater high-temperature strength, alloys. The overall goal is to develop more effective (than currently available) processes to apply highly corrosion-resistant materials to ASME Code-accepted alloys.

#### 2.2.4 New Materials Processes

2.2.4.1 SC(I)-2(D), "Development of Advanced Materials Processes," subcontractor to be determined. This project will focus on the development of new material process methods to develop new material forms and structures involving composites, layered materials, coatings, and so forth. The advancement of materials processing techniques on the AR&TD Materials Program to the stage where industrial interest is sufficient to continue development to commercialization is the aim of this work.

Processes having significant commercial potential will be identified and extended in development through collaborative arrangements with interested industrial organizations.

Table III.2. Research projects for new alloys

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
<b>Advanced Austenitic Alloys</b>						
ORNL-2(B) - Development and Evaluation of Advanced Austenitic Alloys	Oak Ridge National Laboratory (ORNL)	257	250	350	350	250
CU-2 - Mechanical Properties and Microstructural Stability of Advanced Austenitic Alloys	Cornell University (CU)	138	140	140	0	0
USC-2 - Microstructural Studies of Advanced Austenitic Steels	University of Southern California (USC)	a	35	35	0	0
B&W-2 - Evaluation of the Fabricability of Advanced Austenitic Tubing	Babcock & Wilcox (B&W)	26	0	0	0	0
UTN-2 - Investigation of Welding and Joining Techniques for Advanced Austenitic Alloys	University of Tennessee (UT)	148	0	0	0	0
FW-2 - Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coatings, and Claddings	Foster Wheeler Development Corporation (FW)	a	100	100	100	0
SC(I,U)-2 - Steamside Corrosion Tests of Advanced Austenitic Alloys	Subcontractor to be determined	39	100	100	0	0

Table III.2. (continued)

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
SC(I)-2(A) - Procurement of Advanced Austenitic and Aluminide Alloys	Subcontractor to be determined	49	71	75	150	150
	<b>Iron Aluminides</b>					
ORNL-2(F) - Development of Iron Aluminides	ORNL	296	440	500	400	400
ORNL-2(A) - Environmental Effects on Iron Aluminides	ORNL	192	250	250	250	250
INEL-2 - Study of the Influence of Processing on Microstructure and Properties of Aluminides	Idaho National Engineering Laboratory (INEL)	173	175	175	250	250
CSM-2 - Investigation of the Weldability of Iron Aluminides	Colorado School of Mines (CSM)	74	75	75	75	0
HRWL-2 - Secondary-Ion Mass Spectrometry Study of Scales on Iron Aluminides	Harwell Laboratories (HRWL)	15	0	0	0	0

Table III.2. (continued)

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
<b>Coatings and Claddings</b>						
OSU-2 - Fundamental Study of Aluminizing and Chromizing Processes	Ohio State University (OSU)	99	150	150	150	150
WHC-2 - Application of Coatings by the Electro-Spark Deposition Process	Westinghouse Hanford Company (WHC)	106	150	150	150	150
SC(I)-2(C) - Coating and Cladding Process Development	Subcontractor to be determined	0	0	400	400	400
<b>New Materials Processes</b>						
SC-2(D) - Development of Advanced Materials Processes	Subcontractor to be determined	0	300	550	785	830
TOTALS		1,612	2,236	3,050	3,060	2,930

<sup>a</sup> Refers to carryover funding for previous fiscal year.

### 3. CORROSION AND EROSION RESEARCH

#### 3.1 RESEARCH OBJECTIVES

A major objective of this program element is to gain mechanistic understanding of nucleation and growth of protective oxide scales and the degradation of scales in a sulfidation environment. Specifically, attempts will be made to identify alloy modifications and surface treatments that will improve the performance of oxide scales in the environments found in coal combustion and coal conversion processes. Other environments of interest include aqueous and molten salts. In these latter cases, the alloys being tested are the advanced austenitic steels and iron aluminides.

Another objective of this research area is to investigate the mechanisms of erosion, erosion-corrosion, and abrasive wear. Progress in understanding these mechanisms will provide the basis for the development of improved materials subjected to these types of degradation. Most of the projects in this area tend to be fundamental in nature and often incorporate computer modeling studies.

A final area, which is actually the last in a series of ongoing investigations, deals with the development of a data base for refractories used in coal gasification vessels. The study utilizes a thermo-mechanical model to predict failure mechanisms that will help optimize vessel configuration, material property combinations, and heating schedules. Work related to this area has recently been organized under a technology transfer initiative (TCRD-4) and is described in Chap. 4.

All of these fundamental studies are described more fully in the following section and are listed in Table III.3.

#### 3.2 SUMMARIES OF CURRENT AND PLANNED RESEARCH

##### 3.2.1 Fundamental Studies

3.2.1.1 ANL-3. "Corrosion and Mechanical Properties of Alloys in FBC and Mixed-Gas Environments." Argonne National Laboratory. Laboratory oxidation tests have been continued on model base alloys such as Fe-25Cr, Fe-25Cr-20Ni, and Fe-25Cr-6Al (all wt %) in the temperature

range of 500 to 700°C. Oxidation tests are also in progress on alloys modified by (a) alloying additions of 3 wt % Nb or Zr, (b) Nb implantation, and (c) sputter deposits of silicon. Experiments have been carried out to determine the electrical conductivity of thermally grown oxide scales and chemical diffusion of defects in the scales as a function of oxygen partial pressure, temperature, and sulfur level in the gas phase. Additional experiments are under way to determine the solubility and diffusion of sulfur in thermally grown chromium oxide at relatively high oxygen partial pressures and low sulfur partial pressures. An open cell will be used in the near future to evaluate the effect of sulfur in the gas phase on the conductivity, defect structure, and transport properties in thermally grown oxide scales.

3.2.1.2 BCL-3, "Investigation of the Effects of Microalloy Constituents, Surface Treatment, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales," Battelle Columbus Laboratories. The objectives of this program are (1) to gain an improved understanding of the effects of alloying constituents present at low levels on the development and mode of breakdown of protective oxide scales in conditions representing those encountered in combustion and gasification processes at 500 to 700°C; and (2) to achieve better control over the growth of scales which will contribute to improvements in long-term, high-temperature corrosion resistance of heat exchanger and heat recovery materials.

3.2.1.3 CWR-3, "Investigation of the Effects of Microalloy Constituents, Surface Treatment, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales," Case Western Reserve University. The focus of the current program is to obtain a better understanding of material behavior in fossil energy environments. The particular emphasis is on the protectiveness of oxide scales formed in atmospheres containing high  $P_{S_2}/P_{O_2}$  ratios. The iron-based alloys Fe-25Cr, Fe-25Cr-20Ni, and Fe-25Cr-6Al (all in wt %) are base alloys for this investigation. The first two alloys are  $Cr_2O_3$  formers while the third is an  $Al_2O_3$  former. Very severe atmospheres were employed in the initial experiments to help understand basic

mechanisms; further experiments are being devoted to milder and more realistic atmospheres.

3.2.1.4 UES-3, "Investigation of the Effects of Microalloy Constituents, Surface Treatments, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales," Universal Energy Systems. The primary objective of this program is to understand and gain control over the factors that promote the formation of adherent corrosion-resistant protective chromia and alumina scales for long-term application in coal combustion and gasification environments. It has been planned to achieve this objective by investigating the effects of minor alloy additions, surface pretreatments, and the oxidation conditions on the formation and breakdown of chromia and alumina scales in environments containing oxygen and sulfur. The temperatures of interest are in the range of 500 to 700°C, and the partial pressures of oxygen and sulfur of the order of  $10^{-20}$  and  $10^{-8}$  atm respectively. To identify the steps of scale breakdown, pre-oxidized samples are exposed to atmospheres of oxygen and sulfur for different lengths of time. A variety of surface analytical instruments is used to characterize the scale and substrate which will help understand the mixed-gas corrosion process.

3.2.1.5 UTN-3, "Aqueous Corrosion of Iron Aluminides," The University of Tennessee. The purpose of this project is to study the aqueous corrosion characteristics of iron aluminides. The initial effort has primarily entailed generation and analyses of cyclic anodic polarization curves in acid, neutral-chloride, and basic solutions. It has also involved determinations of average corrosion rates in selected systems by two electrochemical methods: Tafel extrapolation of cathodic polarization curves, and the use of small-potential sweeps through the corrosion potential with subsequent statistical analyses. Future evaluations will involve selected mass-loss immersion tests.

3.2.1.6 UCIN-3(A), "Molten Salt-Induced Hot Corrosion of Nickel-Iron Aluminides," University of Cincinnati. The objective of this work is to evaluate the molten salt-induced hot corrosion of nickel-iron and iron aluminides. If these aluminides are to be used in fossil energy

conversion and utilization systems, they must exhibit resistance to mixed sulfidation/oxidation attack and severe corrosion in the presence of molten salts at elevated temperatures. The specific alloys to be used in this study are  $(\text{Ni, Fe})_3\text{Al}$ ,  $\text{Fe}_3\text{Al-2Cr}$ , and  $\text{Fe}_3\text{Al-5Cr}$ . A nickel aluminide ( $(\text{Ni}_3\text{Al})$ ) will be used as the standard for the corrosion tests. The hot corrosion rate shall be evaluated from the weight change as a function of time. The corrosion product shall be characterized by (X-ray) diffraction analysis, scanning electron microscopy, and energy dispersive analysis of X-ray (EDAX). Both the surface morphology and cross-section microstructures will be characterized.

3.2.1.7 LBL-3, "Studies of Materials Erosion in Coal Conversion and Utilization Systems," Lawrence Berkeley Laboratory. The purpose of this work is to gain an understanding of the erosion of material surfaces by small solid particles carried in gas and liquid carriers. The materials are tested over a range of conditions that simulate portions of the operating environment of containment surfaces in coal gasification, liquefaction, and fluidized bed combustion processes. The effects of material properties, microstructures, and compositions on their erosion behavior are being investigated. The effects of elevated-temperature corrosion in combination with the erosion are studied to determine the mechanisms and rates of the combined surface degradation modes.

3.2.1.8 ORNL-3(B), "Responses of Metallic and Oxide Scales to Deformation," Oak Ridge National Laboratory. The purpose of this study is to investigate the processes of corrosion, erosion, and erosion-corrosion in coal combustion and conversion environments. As part of this work, in situ scanning electron microscopy studies of the erosion, corrosion, and simultaneous erosion and corrosion of hot metallic samples are being performed. Fundamental studies are currently being conducted on mechanisms of erosion and corrosion, and long-range plans call for studies of erosion-corrosion. One current study involves determination of the variation in hardness beneath the surface of four aluminum

alloys that have been subjected to multiple impacts by spherical erosive particles. Another study involves similar hardness measurements on annealed 1100 aluminum samples that were exposed to erosive particle impacts at a level below that required to reach steady state conditions. A third study involves use of the erosive particle gun to impact the surface of previously oxidized materials that have small differences in base metal composition. A cooperative study of erosion-corrosion of selected materials has been initiated with Lawrence Berkeley Laboratory.

3.2.1.9 UCB-3, "Solid Particle Erosion in Turbulent Flows Past Tube Banks," University of California, Berkeley. The purpose of this work is to provide knowledge, both experimentally and numerically, about particle-laden erosive flows in tube banks. In the experiment, the flow of air is directed at high speeds through a vertical duct with two in-line tubes of discretely variable spacing aligned normal to the flow. The air carries a dilute concentration of glass beads having a nominal diameter of 97  $\mu\text{m}$ . The speed and turbulence levels of the air approaching the tubes can be altered to investigate their respective influence on particle flux to the tube surfaces. In addition to particle flux, the study calls for measuring particle and fluid-phase velocities using a laser-Doppler velocimeter. The numerical simulation has two principal objectives: (1) to predict as validation test cases the one- and two-tube configurations investigated experimentally, (2) to extrapolate the use of the validated numerical procedure to predict particle-laden gas flows in tube banks. In addition, a new apparatus for developing experimental techniques to study fluidized particle flows around tubes has been devised. The apparatus is very simple to construct and allows some of the main fluid mechanic features of fluidized beds to be clearly visualized and quantified optically.

3.2.1.10 UND-3, "A Study of the Correlation of Materials Structure with Flow Characteristics of Erosive Particles," University of Notre Dame. This research is designed to provide a systematic investigation of the effects of materials properties and experimental variables on the rebound directions and velocities of erodent particles. The

general approach is to develop computer models for the impact of spherical and angular particles, and to compare the predictions with experimental measurements of both single- and multiple-impact rebound parameters. The project will also probe the question of the effects of various strengthening mechanisms on the dynamic flow stress of metals, which serves as the major material variable used as input for the computer rebound models. The project is primarily intended to develop computer models which can be used to predict the direction and velocity of rebound of a particle from a material, which is important in other programs aimed at computation of the flight path of particles through turbine engines. The rebound problem is also of interest from a purely scientific point of view, and because of the relationship between the energy lost and the amount of material removed by a particle during impact. The computer models being developed will take into account several effects neglected in previous models, and will be used to concentrate primarily on the rebound problem. The project will include experiments in which rebound velocity measurements are made during both single- and multiple-particle impact.

3.2.1.11 ORAU-3, "Studies of Erosion and Erosion-Corrosion of Advanced Alloys," Oak Ridge Associated Universities. The goal of this project is to study the erosion-corrosion of various metals and metal alloys using the specially modified scanning electron microscope as well as the mechanical properties microprobe. Specific materials to be investigated include: aluminum alloys, copper, nickel, and iron aluminides. The impact response of these materials will be related to particle velocity and substrate temperature.

3.2.1.12 SC(I,U)-3, "Study of Moisture-Induced Embrittlement of Iron Aluminides," subcontractor to be determined. It was recently discovered that the ductility of iron-aluminide alloys is reduced in the presence of moisture, at room temperature, apparently due to hydrogen embrittlement. The goal of this research is to investigate the mechanism of embrittlement in this class of alloys and determine the conditions under which the mechanism is operative. It is expected that the study will be experimental in nature, involving various

tests, and that the results will be analyzed in ways to help understand the mechanism.

3.2.1.13 UCIN-3, "Study of Particle Rebound Characteristics and Material Erosion at High Temperatures," University of Cincinnati. The objective of this research is to investigate the basic erosion processes and fluid mechanics associated with material degradation in the components of various coal conversion and utilization systems. The understanding of erosion patterns and rates will be enhanced through a study of the rebound characteristics of particles impinging various surfaces and through the measurement of erosion rates of materials exposed to high temperatures. The overall goal is to develop a quantitative model, which will facilitate the prediction of erosion in systems operating in particulated environments. The experimental set-up consists of an erosion wind tunnel, a laser Doppler velocimeter system, a data acquisition system, and a particle feeder.

3.2.1.14 NIST-3, "Mechanisms of Galling and Abrasive Wear," National Institute of Standards and Technology. The successful commercial development of direct coal-fueled diesel engines depends on solving severe wear problems that are not encountered with present day oil-fueled engines. The purpose of this program is to develop a fundamental understanding of the processes and mechanisms that are responsible for wear at the critical piston ring/cylinder wall contact. Particulate matter both from the raw fuel and from combustion products enters the piston ring/cylinder wall contact region and causes rapid wear as a result of direct abrasion of the ring and cylinder wall materials and/or by interfering with the normal lubrication process. In this program, analyses and tests are carried out on raw fuel materials and combustion particulates to determine their abrasion characteristics. Laboratory wear tests are conducted under carefully controlled conditions that are consistent with those occurring at the piston ring/cylinder liner contact in the diesel engine. The effects of test conditions, different types of particulate materials, different lubricants and lubricant additives, and various specimen materials are studied.

3.2.1.15 MIT-3, "Material Data Base Development for Refractories,"  
Massachusetts Institute of Technology. The objective of this task is to study the failure mechanisms of refractory-brick-lined coal gasification vessels under transient temperature loadings. A thermomechanical model, which includes cyclic multiaxial nonlinear constitutive law, temperature-dependent heat conduction, and temperature-dependent creep laws, has been developed for refractory brick and mortar. The model has been implemented in a finite-element program for predicting the stress and strain distributions in brick-mortar linings during the heatup and cooldown cycles. Through simulation and parameter studies, design recommendations will be made for vessel configuration, material property combinations, and optimum heating schedules.

Table III.3. Research projects for corrosion and erosion of alloys

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
<b>Fundamental Studies</b>						
ANL-3 - Corrosion and Mechanical Properties of Alloys in FBC and Mixed-Gas Environments	Argonne National Laboratory (ANL)	316	320	320	400	400
BCL-3 - Investigation of the Effects of Microalloy Constituents, Surface Treatment, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales	Battelle Columbus Laboratories (BCL)	a	0	0	0	0
CWR-3 - Investigation of the Effects of Microalloy Constituents, Surface Treatment, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales	Case Western Reserve University (CWR)	a	0	0	0	0
UES-3 - Investigation of the Effects of Microalloy Constituents, Surface Treatments, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales	Universal Energy Systems (UES)	a	0	0	0	0

Table III.3. (continued)

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
SC(I,U)-3(B) - Fundamental Corrosion Studies in Fossil Energy Environments	Subcontractor to be determined	0	186	250	300	300
UTN-3 - Aqueous Corrosion of Iron Aluminides	University of Tennessee (UTN)	49	50	50	0	0
UCIN-3(A) - Molten Salt-Induced Corrosion of Iron Aluminides	University of Cincinnati (UCIN)	a	0	0	0	0
LBL-3 - Studies of Materials Erosion in Coal Conversion and Utilization Systems	Lawrence Berkeley Laboratory (LBL)	247	250	250	250	250
ORNL-3 - Responses of Metallic and Oxide Surfaces to Deformation	ORNL	192	250	250	300	300
UCB-3 - Solid Particle Erosion in Turbulent Flows Past Tube Banks	University of California Berkeley (UCB)	a	0	0	0	0
UND-3 - A Study of the Correlation of Materials Structure with Flow Characteristics of Erosive Particles	University of Notre Dame (UND)	47	0	0	0	0

Table III.3. (continued)

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
ORAU-3 - Studies of Erosion and Erosion-Corrosion of Advanced Alloys	Oak Ridge Associated Universities (ORAU)	a	0	0	0	0
RPI-2 - Study of Moisture-Induced Embrittlement of Iron Aluminides	Rensselaer Polytechnic Institute (RPI)	59	60	60	60	0
UCIN-3 - Study of Particle Rebound Characteristics and Material Erosion at High Temperatures	University of Cincinnati (UCIN)	109	110	110	125	125
NIST-3 - Mechanisms of Galling and Abrasive Wear	National Institute of Standards and Technology (NIST)	74	125	125	125	125
MIT-3 - Material Data Base Development for Refractories	Massachusetts Institute of Technology (MIT)	a	0	0	0	0
TOTALS		1,093	1,351	1,415	1,560	1,480

<sup>a</sup> Refers to carryover funding from previous fiscal year.



## 4. TECHNOLOGY DEVELOPMENT AND TRANSFER

### 4.1 OBJECTIVES

Technology assessments are performed on the Fossil Energy AR&TD Materials Program to identify existing materials problems or those emerging within the fossil energy technologies, and define the research areas needed to solve these problems. Emphasis will also be directed toward early commercial availability of new materials, and enhanced U.S. technological competitiveness in a world market. The current assessment projects deal with the applicability of structural ceramic composites to gas turbines, on-site examination and failure analysis of components at a coal conversion facility, and the long-range materials research and development needs for Fossil Energy.

The objective of the technology transfer part of the program element is to make industry more aware of the developments on the AR&TD program and to encourage early participation by industry in the development of new materials. Such participation would encourage early commercialization of useful and reliable products. Other technology transfer mechanisms to help the U.S. maintain a technical edge in material science include: outreach programs to seek corporate partners, cooperative process scaleups or application evaluations, and the establishment of consortia. Current technology transfer projects on the program include the development of software to analyze refractory linings, the compilation of data concerning the performance of various materials in coal liquefaction environments, and a materials and components newsletter. Also included are two proposed technology transfer projects (for FY 1991) dealing with iron aluminides, and advanced austenitic alloys.

The specific activities associated with these program elements are described in the following section and are listed in Table III.4.

## 4.2 SUMMARIES OF CURRENT AND PLANNED ACTIVITIES

### 4.2.1 Technology Assessment

4.2.1.1 BCL-4, "Materials and Components in Fossil Energy Applications Newsletter," Battelle Columbus Laboratory. The DOE Newsletter on *Materials and Components in Fossil Energy Applications* is intended as a vehicle to provide timely dissemination of information concerning developments in, or performance results of, materials and components in conventional or new processes for the utilization of coal, or for the conversion of coal to other energy forms. In recent years, emphasis has been placed on the direct utilization of coal as a chemical feedstock or as a fuel, rather than for providing a substitute for natural gas. Process efficiency and compliance with present and anticipated environmental regulations are two of the most important factors driving developments, and strongly influence not only new processes, but also existing systems.

4.2.1.2 NIST-4, "Assessment of Fossil Energy Materials Research Needs," National Institute of Standards and Technology. The purpose of this twelve-month study is to identify long-range materials research and development needs and opportunities as they impact evolving fossil energy technologies. The needs and opportunities that are identified should be appropriate for future research on the AR&TD Materials Program. The assessment is being conducted in three phases: (1) review of prior assessments of fossil materials needs, (2) review of current fossil energy program needs, and (3) study conclusion and coordination.

4.2.1.3 ORNL-4(B), "Coal Conversion and Utilization Plant Support Services," Oak Ridge National Laboratory. The purpose of this work is to supply support services to the Energy Technology Centers (Morgantown and Pittsburgh) and the Advanced Coal Liquefaction Research and Development Facility at Wilsonville, Alabama. The support is in the areas of materials selection, evaluation, testing, on-site examination, and analysis of failed components. In addition to providing a valuable service to the operators of these facilities, this task assures that the Fossil Energy Materials Program staff is kept abreast of the

materials problems that are being encountered, and provides input to the ongoing assessment of materials research needs based on actual operating experience.

4.2.1.4 SOR-4, "Reference Book on Performance of Materials in Coal Liquefaction Environments," G. Sorell. Through the auspices of The Materials Properties Council, Inc. (MPC), several government, industrial, and university organizations are contributing information and data on materials performance in coal liquefaction environments for inclusion in a reference book. Such a book is not only desirable but is sorely needed as an archival reference to the great body of information developed over the past several years. A consultant (G. Sorell) will collect information (chapters of the book) from the various authors, edit the submitted information, and compile it into a single reference source for subsequent publication.

#### 4.2.2 Technology Transfer

4.2.2.1 3M-4, "Fabrication of Full-Scale Fiber-Reinforced Hot-Gas Filters by Chemical Vapor Deposition," 3M Company. The purpose of this project is to scale up the Chemical Vapor Infiltration (CVI) process developed at ORNL for fabricating ceramic fiber-ceramic matrix composites filters. The goal is to use this scaled-up CVI process to produce composite filters that have the requisite strength and toughness, but which also have sufficient porosity to be permeable to gas streams and the appropriate size and distribution of porosity to be an effective filter. A practical process for fabricating porous ceramic fiber-ceramic matrix candle filters (full-size) with increased surface area will be developed in collaboration with ORNL.

4.2.2.2 TCRD-4, "Development of User-Friendly Software for the Thermo-mechanical Stress Analysis of Refractory Systems," Tennessee Center for Research and Development. The objective of this work is to develop user-friendly software within the UNIX environment which will enable the non-expert using a work station to perform thermomechanical stress analysis of refractory linings for the user's specific design and analysis problems. The user-friendly software system will allow users to access design guidelines and to develop preliminary refractory

lining designs, to perform finite element analyses for final designs, and to facilitate the modification of existing or the addition of new capabilities through a modular program structure.

4.2.2.3 CARB-4, "VLS SiC Process Development," Carborundum Company.

This work will transfer to industry a specific technology developed on the AR&TD Materials Program for the production of silicon carbide whiskers. The vapor-liquid-solid (VLS) process was developed at Los Alamos National Laboratory for the growth of silicon carbide whiskers of up to 75 mm in length. Whisker length can be reduced by subsequent processing. This work will develop the VLS into an engineering-scale (45 to 226 kg/year) process that will enable the U.S. industrial sector to commercialize the process for the production of whiskers for the reinforcement of structural ceramic composites. Request for Proposal (RFP) No. SD861-86 was issued on July 5, 1989, to invite proposals to conduct the work. The successful proposal was submitted by the Carborundum Company, and we anticipate the work will be initiated in the third quarter of FY 1990.

4.2.2.4 SC(I)-4(B), "Development and Evaluation of Ceramic Composites for Gas Turbine Components," subcontractor to be determined.

The Babcock and Wilcox Company with assistance from Solar Turbines, Inc., recently completed an assessment of the applications of structural ceramic composites in gas turbines, including direct coal-fired turbines. The conclusions of this study were that ceramic composites would be of considerable value for use as turbine nozzle vanes and as rotor blades. Based on that assessment, a request for proposal will be issued to develop and evaluate these components. The development will include the identification of appropriate materials of construction and processing methods, and the establishment of performance criteria for the materials. The evaluation of materials will determine if performance criteria were met.

4.2.2.5 SC(I)-4(C), "Evaluation of the Fabricability of Iron

Aluminides," subcontractor to be determined. This project addresses the problems associated with fabricating tubing, sheets, and other product forms from iron-aluminide alloys. The specific alloys that will be investigated are being identified in project ORNL-2(F),

"Development of Iron Aluminides." The scope of the planned project consists of melting experimental alloys, conditioning ingots and forging of ingots into extrusion billets, and producing seamless tubing. Plate and sheet materials will also be produced to further evaluate the fabricability of this material. Samples of the product forms produced on this project will be used in complementary tasks to examine the mechanical behavior, weldability, and corrosion behavior of the material.

4.2.2.6 SC(I)-4(D), "Ceramic Filter Development," subcontractor to be determined. This work will focus on further development and scaling up of the processes using ceramic filaments and forced CVI to fabricate reinforced ceramic filters.

4.2.2.7 SC(I)-4(E), "Ceramic Membrane Development," subcontractor to be determined. Ceramic membranes are presently being developed on the AR&TD Materials Program by the Oak Ridge Gaseous Diffusion Plant. That work is a companion project to work sponsored by the Morgantown Energy Technology Center at ORNL to test these membranes for hydrogen recovery and noxious gas removal from coal gasification streams. This work, to be initiated at an industrial subcontractor, will use and extend the results of the ORNL/ORGDP work to other membrane systems for a variety of gas separation systems. The principal focus of the project will be on hot-gas stream cleanup.

4.2.2.8 SC(I)-4(F), "Technology Transfer - Iron Aluminides," sub-contractor to be determined. As potential applications for the iron aluminides are identified, we will establish cost-shared contracts with industrial organizations to further the development for these specific applications. Although our interest is first for applications in coal technologies, related applications will be considered as well. For example, funding of further development for applications that would assure the introduction of the iron aluminides into the commercial sector would be appropriate for the AR&TD Materials Program.

4.2.2.9 SC(I)-4(G), "Technology Transfer - Advanced Austenitic Alloys," subcontractor to be determined. The advanced austenitic alloys have considerable potential in a variety of high-temperature applica

tions including heat exchanger, or boiler, tubing in advanced combustion systems such as coal-fired power plants and fluidized bed combustors. Applications for these alloys are probably somewhat more limited than they are for the iron aluminide alloys. Therefore, a somewhat different approach will be used in this technology transfer effort. We will attempt to establish a consortium of industrial companies for the purpose of funding work to further demonstrate the potential of these alloys in heat exchangers of advanced combustion systems. The consortium concept allows each member to leverage its funds and to obtain the benefits of a substantial project. Such an effort could be coordinated with organizations such as The Materials Properties Council, Inc., or the Electric Power Research Institute.

Table III.4. Technology development and transfer activities

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
<b>Technology Assessments</b>						
BCL-4 - <i>Materials and Components in Fossil Energy Applications</i> Newsletter	Battelle Columbus Laboratories (BCL)	114	115	115	115	115
NIST-4 - Assessment of Fossil Energy Materials Research Needs	National Institute of Standards and Technology (NIST)	a	0	0	0	0
ORNL-4(B) - Coal Conversion and Utilization Plant Support Services	Oak Ridge National Laboratory (ORNL)	49	100	100	100	200
SOR-4 - Reference Book on Performance of Materials in Coal Liquefaction Environments	G. Sorell (SOR)	a	0	0	0	0
<b>Technology Transfer</b>						
3M-4 - Fabrication of Full-Scale Fiber-Reinforced Hot-Gas Filters by Chemical Vapor Deposition	3M Company (3M)	a	100	200	200	0
TCRD-4 - Development of User-Friendly Software for the Thermomechanical Stress Analysis of Refractory Systems	Tennessee Center for Research and Development (TCRD)	82	100	100	50	0

Table III.4. (continued)

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
CARB-4 - VLS SiC Process Development	Carborundum Company (CARB)	238	250	350	0	0
SC(I)-4(B) - Development and Evaluation of Ceramic Composites for Gas Turbine Components	Subcontractor to be determined	0	240	150	200	250
SC(I)-4(C) - Evaluation of the Fabricability of Iron Aluminides	Subcontractor to be determined	25	100	150	150	100
SC(I)-4(D) - Ceramic Filter Development	Subcontractor to be determined	0	100	250	250	250
SC(I)-4(E) - Ceramic Membrane Development	Subcontractor to be determined	0	100	250	250	250
SC(I)-4(F) - Technology Transfer - Iron Aluminides	Subcontractor to be determined	0	100	250	250	250

Table III.4. (continued)

Research project	Performing organization	Funding (thousands of dollars)				
		FY 1990	FY 1991	FY 1992	FY 1993	FY 1994
SC(I)-4(G) - Technology Transfer - Advanced Austenitic Alloys	Subcontractor to be determined	0	100	250	250	250
SC(I)-4(H) - Technology Transfer - Advanced Materials Processes	Subcontractor to be determined	0	0	0	785	933
MSS-4 - Management, Support Services and Special Studies		635	598	817	825	827
TOTALS		1,143	2,003	2,982	2,640	2,492

<sup>a</sup> Refers to carryover funding from previous fiscal year.



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