

ABSTRACTS

**The
Fourteenth Annual
Conference on
Fossil Energy Materials**

April 24-26, 2000

Knoxville, Tennessee

U.S. Department of Energy
Office of Fossil Energy
Advanced Research Materials

Fossil Energy Advanced Research Materials Program

Welcome to the Fourteenth Annual Conference on Fossil Energy Materials.

The Fossil Energy Advanced Research Materials Program (Program) is highly integrated materials research activity of Fossil Energy's Coal and Advanced Power Systems Program. The objective of the Program is to conduct research and development (R&D) for all advanced coal conversion and utilization technologies. Although the Program is driven by advanced coal technology materials needs, significant benefits are often derived by oil and gas technologies, such as fuel cells, and by non-fossil energy technologies. Research problems related to the more advanced systems and ongoing technology R&D programs are addressed on the Program. As a materials R&D activity focusing on advanced technologies, the Program is directed primarily toward longer-term materials development needs. The Program is aimed at a better understanding of materials behavior in fossil system environments and the development of new materials capable of substantial improvement in plant operations and reliability.

A generic or crosscutting approach is used to ensure that materials are developed to address multiple technologies. For example, our hot-gas particulate filter development is applicable to pressurized fluidized bed combustion, integrated coal gasification combined-cycle, coal combustion, and indirectly fired combined-cycle systems. The more technology specific materials fabrication and manufacturing development, and specific evaluations of materials for these technologies are the responsibilities of the Fossil Energy line programs.

Materials R&D on the Program addresses both structural materials, i.e., materials used for structural components, and functional materials, which have properties important to the performance of a specific process function.

Work on the Program is in progress at national and government laboratories, universities, and private sector companies. The Program features national laboratory-industry partnerships that greatly facilitate the deployment of the materials technology developed on the Program.

We thank you for your interest in the Program and for your participation in this conference.

Conference Chairmen

**R. R. Judkins, Manager
Fossil Energy Program
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General Conference Information

Presentations

- Ě General sessions will be held in Salon C of the Cherokee Ballroom on the Mezzanine of the Hilton Hotel.
- , A buffet and poster session will be held in Salons A and B of the Cherokee Ballroom on Monday and Tuesday evening beginning at 6:30 p.m.

Registration

- Ě Participants and guests may register for the conference on the Mezzanine beginning at 4:00 p.m. Monday afternoon and at 7:00 a.m. Tuesday morning.
- Ě Coffee and refreshments will be provided prior to the start of each morning's session and during breaks.

General

- Ě A list of all conference attendees will be provided. Please check your mailing address for correctness to ensure receipt of any subsequent mailings.
- Ě All messages may be picked up at the conference desk.
- Ě Telephones are located on the Mezzanine next to the main stairs.

Efficient Zirconia Electrolyte Fabrication

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T. L. Starr
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Current yttria-stabilized zirconia (YSZ) electrolyte materials are inefficiently processed or are inefficient in operation. The highest quality material is currently produced by chemical vapor deposition (CVD) at reduced pressures. Such processes are capital and operationally intensive, and thus cannot meet cost goals. More conventional ceramic forming processes cannot produce the purity/quality material desired or cannot produce the thin films that provide for high efficiency. At ORNL we are studying atmospheric pressure CVD techniques that would be significantly less costly and would lend themselves to continuous processing. As an initial step in that work is a thermochemical analysis of atmospheric pressure CVD of YSZ has been performed to explore the variable space of temperature, reactant composition, and deposition efficiency.

Development of NDE Methods for Hot Gas Filters

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Hot gas candle filters are currently under development for hot gas particulate cleanup for advanced coal-based power systems. Ceramic materials are one materials system under development for hot gas filters and include oxide/oxide composites, clay-bonded SiC, recrystallized SiC, and others. One concern at plant shut downs is reliable data on which to base decisions for reusing or replacing hot gas filters as well as possibly predicting remaining service life. The work in this project is directed towards developing nondestructive evaluation (NDE) technology which will allow detection and measurement of life limiting materials characteristics such as cyclic fatigue from the back pressure pulsing, thermal shock, localized cracking, damage from local burning and chemical attack. The study of Lamb waves in an acousto-ultrasound(AU) set up, initiated last year as an NDE method, has been more fully explored this year on a wide variety of rigid ceramic hot gas filter materials which have been exposed to plant conditions at the Power Systems Development Facility(PSDF) located in Wilsonville,Alabama, the Siemens-Westinghouse test facility in Pittsburgh, Pennsylvania, and from the University of Tampere in Tampere, Finland. The filter materials studied have included McDermott Technologies oxide/oxide composites, Honeywell Advanced Composite PRD-66 oxide/oxide composites, Pall 326 and 442T which are clay-bonded SiC, Schumacher TF20 and T10-20 which are also clay-bonded SiC and Coors P-100-A1 which is an alumina composition. The stress wave factor (SWF) data obtained from the AU system has been correlated with strength data when the strength data have been obtained from 4-point bend, C-ring, O-ring compression and internal pressurized bladders. In each case, well-defined correlations were obtained demonstrating a decreasing SWF with decreasing strength. The results of the NDE AU investigations on these hot gas filter materials as well as additional corroborating NDE data from ceramic hot gas filters will be presented.

Solid State Electrolyte Systems

L. R. Pederson, G. W. Coffey, J. S. Hardy, K. J. Kerstetter,
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A planar oxygen separator was constructed using $(\text{SrO})_{0.14}(\text{CaO})_{0.14}(\text{Bi}_2\text{O}_3)_{0.72}$ as the electrolyte, ferritic stainless steel as the electrical interconnect, silver and silver-bismuth oxide cermets as both electrodes, and mica sheet as compression seals. Bismuth oxide electrolytes were prepared by lamination of tape-cast films, nominally 200 microns thick and with 15 cm^2 active surface area per plate. Ferritic stainless steel interconnects, prepared by powder metallurgy as well as by machining, provided a good thermal expansion match to the electrolyte but required a protective coating to remain conductive. At an operating temperature of 750°C , necessary to convert the electrolyte to the most highly conductive form, approximately 50 mL oxygen per minute per plate was produced at a current density of 1 A/cm^2 . Electrode compositions were screened using cyclic voltammetry and current interrupt measurements with an embedded Luggin reference. Silver gave the lowest specific electrode resistance of any tested. Copper and manganese-doped bismuth oxides showed good mixed conductivity but poor electrode stability. Anodic reactions were found to be considerably more sensitive to electrode properties than cathodic reactions.

Two mixed electron and ion conducting electrolyte systems are being developed for possible use as passive oxygen separation membranes and related applications: LaSrCrFe perovskites and ceria-based ceramic composites. Oxygen and electron conductivities, thermal expansion behavior, and fracture toughness were determined as a function of temperature and oxygen partial pressure. Both systems show good stability in a reducing environment. Ceria composites were used successfully to partially oxidize methane to carbon monoxide and hydrogen without membrane degradation.

Ceramic Membrane for High Temperature Hydrogen Separation

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Although many details of our ceramic membranes remain classified, significant progress has been made in removing some of the restrictions. We will review the status of membrane classification and non-proliferation reviews. The major problem requiring attention in the past two years has been evaluating effective methods to eliminate leaks and defects in the membranes. We are now fabricating what appears to be defect-free membranes. In addition, we have membranes which achieve our target permeance of 0.01 std cc/min/sq cm/cm hg. We will discuss the composition and characteristics of our most recent ultra-small pore size membrane. Our current membranes are in the pore diameter range from about 0.7 to 1 nm. At ambient temperature, some of these membranes show carbon dioxide permeance greater than helium by a factor of 2 to 3. We will review some of the data to show variation in the permeance of individual gases as a function of pressure and temperature and the separation factors estimated from these data. The data that we are acquiring is consistent with the 'hard sphere mathematical model' that we have developed for guidance. Now that we routinely are achieving defect-free membranes, we are setting up to make binary gas separation measurements to confirm the results for the individual gas permeance measurement.

**Development of New Hybrid Organic-Inorganic Materials
for Hydrogen Separation Membranes**

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We are preparing new hybrid organic-inorganic materials for hydrogen separation membranes based on functionalized polysilsesquioxanes. These materials exhibit superior thermal and chemical stabilities compared with many of the organic polymers presently used for hydrogen separation membranes. The polysilsesquioxanes used in this study are soluble in organic solvents, yet can possess chemical functionalities as part of the organic groups that can be used to cure thin films into the thermally robust, intractable membranes. The films themselves can be prepared on mesoporous alumina supports by spin coating, spraying, interfacial polymerizations or phase separation processing. The cure behavior, including onset temperatures, and the physical properties of the final material can be engineered through the design of the organic functionality.

Bismuth Oxide Solid Electrolyte Oxygen Separation Membranes

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Doped b-Bi₂O₃ exhibits oxygen ion conductivity that is much higher than yttria-stabilized ZrO₂ (YSZ) up to the maximum operating temperature of about 800°C. The b-phase of Bi₂O₃ is formed by partial substitution for the bismuth atoms by divalent alkaline earth ions such as calcium, strontium, and barium. The conductivity increases by nearly ten-fold due to a phase change in the temperature range of 560°C to 745°C, depending upon the amount and type of dopant in the composition. At the transformation temperature, the low-temperature b₂ phase transforms to the high-temperature b₁ phase. When this transformation occurs, the ionic conductivity of b-Bi₂O₃ is 35 to 65 times greater than that of YSZ at the same temperature. Test results for baseline samples containing 28 mol% dopant (CaO, SrO, or BaO) were presented in the previous report. New compositions containing mixed alkaline earth dopants, different amounts of dopants, and compositions with additional additives have been prepared and evaluated to compare properties with the baseline samples. While a number of factors affected the observed properties, the most important variables influencing the conductivity level and the transformation temperature were the type and the amount of the alkaline earth dopant in the composition. The thermal expansion of a number of the b-Bi₂O₃ compositions was measured to temperatures above the b₂/ b₁ phase transformation temperature. There is an abrupt increase in the linear expansion of about 0.3% in these materials at the phase transformation temperature. The thermal expansion will be an important factor to consider in the design of an oxygen separation device because of the need for compatibility with other materials in the device assembly. Mechanical durability will also be an important consideration in the device design. Some preliminary mechanical property measurements have been made on several of the b-Bi₂O₃ compositions. The modulus of rupture was measured in 4-pt. bending. Samples showed a range of fracture strengths from less than 20 to about 56 MPa.

**Characterization of Ceramic Hydrogen Separation Membranes
with Varying Nickel Concentrations**

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Thin and dense ceramic membranes fabricated from mixed electronic and protonic conductors may provide a simple, efficient means for separating hydrogen from gas streams. Ceramic hydrogen separation membranes (developed at Argonne National Laboratory) in the stoichiometric form $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_3$ doped with various nickel concentrations were characterized utilizing X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM)/ energy dispersive spectrometer (EDS), and atomic force microscope (AFM). Characterization was performed at room temperature, 550 °C, 650 °C and after hydrogen exposures. Migration of nickel to the surface, and changes in both elemental composition and oxidation states of elements were observed at elevated temperatures. The concentration of nickel has a significant effect on the surface morphology and roughness. Significant changes in the surface composition of the membranes were also observed after hydrogen permeability tests conducted at high pressure and high temperature.

Development of Alloys for Steam Generators

R. W. Swindeman, P. J. Maziasz, and I.G. Wright
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This presentation summarizes past selection and development of steam generator materials for advanced and ultra supercritical (USC) plants, the materials currently available for such applications and their limitations, and some considerations for future materials development efforts. The U.S. developed the Eddystone #1 and Philo 6 USC plants in the 1950's, EPRI led the Phase 2 USC development effort during the 1980's, and USC efforts during the 1990's have been pushed mainly by the European and Japanese materials programs. Materials research programs directed toward USC plants have provided several different advanced martensitic/ferritic steels and austenitic stainless steels and alloys. Progress has also been made on nickel-based alloys, on coatings and claddings of corrosion-resistant materials, and on development of advanced oxide-dispersion-strengthened (ODS) materials. However, there are still major unresolved issues that need to be addressed by continued materials research programs around the world to provide materials that will operate confidently above 800°C in USC plants.

Cladding with Fe-Al Alloys

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A thermal spraying technique, wire arc spraying, was used to produce Fe-Al alloy deposits on carbon steel surfaces. The consumable material used in the arc spraying was an Fe-Al composite wire with a nominal chemical composition of Fe-26Al-0.25Mo-0.25Zr-0.1C, wt%. The carbon steel surfaces were prepared so that the deposits would spontaneously detach after they were built up to thicknesses of 1-2 mm. The deposits were made under various conditions using either air or nitrogen as a propellant/shielding gas. Chemical analysis showed that all of the deposits experienced a loss of Al relative to the wire composition. The deposits were also enriched in O and N. Metallographic examination of the deposits showed they each contained oxide phases distributed throughout their thicknesses. The deposits made in the presence of air contained higher amounts of entrained oxides. Microchemical analysis indicated that the most prevalent oxide in the deposits was Al_2O_3 . Smaller amounts of Fe oxides were also observed. Microchemical analysis also indicated that substantial alloying of the Fe and Al of the composite wire occurred during the spraying process. No unreacted Al particles were found in the deposits, but occasionally particles of unreacted Fe were observed. The environmental resistance of the deposits was evaluated by exposing specimens to still air at 500°C and 900°C both before and after a pretreatment exposure of 1000°C for 1 h in air. Overall, the weight gains experienced by these specimens were several times greater than those expected in monolithic specimens of identical composition. Also, in terms of weight gain, there was no significant difference between using air or nitrogen as a propellant for the arc spraying process.

Solidification Behavior and Weldability of Haynes HR-160

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The solidification and welding metallurgy of Haynes Alloy HR-160, a nickel-cobalt-chromium based superalloy containing relatively high levels of silicon (~2.6%) designed for use in aggressive high temperature environments, has been the focus of current research. HR-160 type alloys containing different levels of silicon (2.0%, 3.9%) and iron (0%, 3.9%) were designed to investigate the effects of silicon and iron on weldability. Production HR-160 was used as a baseline. Fusion zone solidification crack susceptibility was quantified using the Sigmajig test. Results show that the alloys containing low amounts of silicon have the best cracking resistance while the high-silicon alloys have the worst cracking resistance. The effect of iron appears complex; the high-silicon, high-iron alloy exhibited better crack resistance than the alloy containing high levels of silicon with no iron. Microstructural analysis revealed a eutectic-type interdendritic phase rich in silicon and titanium. The volume fraction of the phase increased with increasing silicon content. Compositional traces showed that silicon and titanium preferentially segregated to the interdendritic regions while iron segregated slightly more to the matrix. The relatively high cracking susceptibility of the high-silicon alloys is attributed to the segregation of silicon and titanium to the interdendritic regions and to the presence of a large quantity of enriched interdendritic liquid at the time of final solidification.

Reduction In Defect Content Of ODS Alloys

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The overall goal of the current programme of work is to determine the nature and origin of various kinds of microstructural defects in Mechanically Alloyed (MA) Oxide Dispersion Strengthened (ODS) Alloys. A principal aim is to determine means to minimize or control the incidence of these defects and thereby their influence on alloy service performance.

Previous studies have demonstrated that fully consolidated MA materials can contain a range of defects originating from different stages in the powder production and consolidation process. These defects include inhomogeneous particle distributions (inhomogeneous MA), intrusions (retained powder fragments), porosity and incomplete secondary recrystallisation (retained fine grained stringers). All such defects may play a role in determining both the release condition and final high temperature service performance of such alloys, though some may prove more deleterious than others under specific service conditions.

The current work has continued to develop cross-comparisons between the microstructures developed in an MA ODS Fe₃Al intermetallic alloy and those in PM 2000 (a fully commercial ODS FeCrAl) at all stages between fully processed MA powders and the fully consolidated heat treated alloys. Principal concerns in the study have been to establish details of the nature of the secondary recrystallisation process in the MA ODS Fe₃Al alloy and way in which this is influenced by specific microstructural features, such as oxide stringers and other microstructural inhomogeneities. From the results it is clear that the final secondary recrystallised microstructures which can develop in the ODS Fe₃Al alloy are distinguished from those in PM 2000 by factors which can include the detailed size and spatial distribution of the coarser oxide particles and differences in the homogeneity of MA which exist between the two types of fully processed powders.

Oxide Dispersion Strengthened Fe₃Al-Based Alloy Tubes

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ODS-Fe₃Al thin walled tubes, using powder extrusion methodologies, are currently being developed for eventual use at operating temperatures of up to 1100°C, as heat exchanger tubes, in the power generation industry. A particular 'in service application' anomaly of Fe₃Al-based alloys is that the environmental resistance is maintained up to 1200°C, well beyond where such alloys retain sufficient mechanical strength. Oxide dispersoids are therefore employed to improve high temperature mechanical strength, but their incorporation invariably results in an extremely fine grain size in as-processed materials. Grain boundary creep processes at service temperatures, of such fine-grained materials, are thus anticipated to be the dominant failure mechanism.

This current presentation will detail our current progress on ODS-Fe₃Al processing methodologies and microstructural development efforts to 1) manufacture 1-3/8 to 2-1/4' OD, 1/8-3/8" wall thickness, tubes *via* single step extrusion consolidations, to 2) increase strength at temperature employing Y₂O₃ oxide dispersion strengthening (ODS), and 3) enhancing the as-processed grain size in ODS-Fe₃Al rods/tubes by selective recrystallization schemes in highly textured rods/tubes. Such procedures routinely produce large through-thickness grain sizes, typically of the order of milli-meters, suitable for 'in-service' creep resistance.

Low-Cost Processing Technique For Solid State Devices

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The cost of fabricating solid state devices needs to be lowered. For instance, the manufacturing cost of high-temperature solid oxide fuel cells (SOFC) is significantly higher than their gas-turbine counterparts. Therefore a major impetus for commercialization of SOFC is to reduce their processing costs. To overcome this major technical challenge a one-step hot-pressing process is proposed as an alternative less expensive technique to fabricate such devices. The process will be engineered to obtain an ultimate structure that contains the thin-dense solid electrolyte in intimate contact with the porous electrodes, anode and cathode, on the two opposite sides of the electrolyte. A planar solid oxide fuel cell will be fabricated in one step to demonstrate viability. However, it is projected that several cells could be fabricated at a time, further reducing cost. Additionally if successful, the technique could also be used for processing intermediate temperature solid oxide fuel cells, oxygen pumps, sensors and other solid-state ceramic electrochemical devices. Process development and preliminary data and analysis carried out in determining the hot pressing parameters will be presented and discussed.

Modeling of Atmospheric CVD for Zirconia Electrolytes

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**T.M. Besmann and V. Varanasi,
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High-temperature solid-oxide fuel cells (SOFC) have strong potential for large-scale production of electrical energy from fossil fuels. While commercialization of this technology has begun, the high cost of these systems is still a barrier to implementation. Our research addresses the manufacture of a key component of these systems – the solid oxide electrolyte – and aims to reduce its cost through development of an improved, ambient pressure method for chemical vapor deposition (CVD) of zirconia films.

There are two critical requirements for successful, ambient pressure CVD of solid oxide electrolyte films: maintain uniformity in thickness and composition over a reasonably large substrate, and avoid gas-phase nucleation that degrades film quality. Our research approach addresses both of these requirements and is based on the unique characteristics of a stagnation point flow CVD reactor.

In this paper we review the use of stagnation point flow geometry for CVD of semiconductor thin films and show that the process has demonstrated the requirements indicated above. Also, we report initial results of a one-dimensional model of a stagnation point flow CVD system for zirconia. This model is being used to design and optimize an experimental reactor at ORNL.

Performance Evolution of Thin-Film Multi-Layer Packages

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In recent years, we have learned how to make fuel cells; the challenge now is how to make them work - work well enough and long enough to be technically feasible and economically competitive. The feasibility of doing that depends on the long-term performance of fuel cells under operating conditions. Presently, performance (usually measured by voltage-current metrics) typically decreases with time, often quite sharply, especially for high temperature SOFCs. This decrease is driven by changes in the materials used to make the cells, and in the interfaces between them, what can be called "material state evolution." The goal of the present work is to develop understandings and models of material state evolution that relate those material processes to the performance of fuel cells and stacks. Particular attention is being paid to the relationship of material state evolution kinetics to processing and manufacturing options. Modeling approaches are based on adaptations of "critical element" concepts developed as part of the CFCC and Fossil Energy programs.

Gas Separation Using a Carbon Fiber Composite Molecular Sieve

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A novel monolithic carbon adsorbent material has been developed and its use for the separation of gasses has been demonstrated. Because the material exhibits a continuous carbon skeleton it is electrically conductive, allowing for the electrical stimulation of desorption of adsorbed gasses. This phenomena has been utilized in a gas separation process we have named *Electrical Swing Adsorption*, ESA, which is analogous to PSA and TSA except that the process is driven by swinging and applied voltage on the adsorbent rather than pressure or temperature. Recently, we have been investigating the modification of our adsorbent monoliths to increase their selectivity for O₂/N₂ separations. The separation of O₂/N₂ is kinetic and, therefore, the size of the pores must closely match the size of the O₂/N₂ molecules. A carbon vapor deposition process has been used to reduce the micropore size of the material. Two mechanisms of pore size reduction are postulated: (i) the formation of a microporous carbon membrane over the porous fibers, or (ii) the partial “plugging” of pore openings to form “inkbottle” pores. The development of our novel adsorbent carbon and the ESA process will be reviewed and preliminary data on the modification of the micropore structure reported.

Improved Creep Resistance for Gas Turbine Recuperators

P. J. Maziasz, R. W. Swindeman, (Oak Ridge National Laboratory), M. Preston Montague, P. F. Browning, (Solar Turbines, Inc.), and J. F. Grubb, R. Klug, (Allegheny-Ludlum, Allegheny-Teledyne Co.)

Primary surface recuperators (PSRs) are heat-exchangers, typically made from type 347 austenitic stainless steel foil, which boost the efficiency of land-based gas turbines. Recuperators are also an essential technology for advanced microturbines. Current RSPs for mid-sized engines using type 347 stainless steel foil are limited to operation at or below about 660°C. This team-effort project has demonstrated significant improvements in creep resistance at 650-700°C in lab-processed material with critical changes to the processing conditions, but to date has not achieved the same results in commercial-scale industrial foil processing. Detailed analysis of microstructural changes during processing and correlation with creep behavior suggests the critical processing parameters necessary for good creep-resistance in 347 stainless steel. Similar lab-scale experiments on several other stainless steels and alloys with more Cr for better oxidation-resistance at higher temperatures also indicate that processing/microstructure control is essential to obtain good creep-resistance. The objective of this project remains to refine this understanding of processing, microstructure and properties and apply it to commercial-scale foil products.

Processing and Properties of Molybdenum Silicide Intermetallics Containing Boron

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Molybdenum-Silicon-Boron intermetallics containing phases such as Mo_5Si_3 (T1), Mo_5SiB_2 (T2), and Mo_3Si are potentially highly oxidation resistant materials of interest for hot components in fossil energy conversion and combustion systems. Since their melting points are in excess of 2000°C , they have potential as ultra-high temperature structural alloys. Alloys with the compositions Mo-12Si-8.5B (at. %) were prepared by arc-melting and drop-casting. They consisted of approximately 40 vol.% α -Mo particles in a matrix of 30 vol.% T2 and 30 vol.% Mo_3Si and their room temperature fracture toughness was on the order of $10 \text{ MPa m}^{1/2}$. Their high temperature mechanical properties at up to 1400°C were explored by flexure and compression tests, as well as by tensile creep tests. A typical creep rate at a temperature of 1200°C and an applied stress of 100 MPa was 10^{-7} s^{-1} , and the stress exponent was on the order of 3.

In order to obtain improved oxidation resistance, alloys with higher Si concentrations than those in Mo-12Si-8.5B were prepared by arc-melting and drop-casting. However, these castings tended to contain macro-cracks. Therefore, powder-metallurgical techniques were used to fabricate alloys with higher Si concentrations. Alloys with different α -Mo contents were prepared either from elemental powders or from powders obtained by crushing cast ingots. The powders were consolidated by hot isostatic pressing (HIP) or hot-pressing. Even very coarse pre-alloyed powders (0.85 mm = size = 2 mm) were fully densified by HIPing at 1600°C and 200 MPa. The advantages and disadvantages of the different approaches will be discussed. As expected, the room temperature flexure strengths and fracture toughness values decreased with decreasing α -Mo content. The decreases in strength and fracture toughness were accompanied by an increase in the oxidation resistance.

Fabrication of Tubing from High-Strength Alloys

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Several alloys, including high-strength stainless steels, Alloy 803, and Thermie alloy are being considered as super heater tubing for power plant concepts in support of Vision 21. In addition to conventional alloys stated above, effort is also underway to look at oxide dispersion-strengthened alloys based on iron aluminide. This presentation will describe the processing details used in the fabrication of these tubes. Chemical analysis and microstructure of the tubes will also be discussed.

**Investigation Of Aligned Microstructures Of Cr-Ta Composites
Reinforced By Cr₂ta Laves Phases**

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The Cr-Ta alloy with an eutectic structure has a good combination of high strength and oxidation resistance at elevated temperatures up to 1200°C. It is an ideal candidate for ultra-high temperature applications. However, the material shows low ductility and fracture toughness at room temperature. In the present work, the process of directional solidification (DS) to obtain an aligned eutectic microstructure of a binary eutectic Cr-Ta alloy was studied in order to improve the ductility and fracture toughness. The relationship between the microstructure and chemical composition was investigated. The eutectic composition of the binary Cr-Ta alloy was determined to be Cr-9.4 at.% Ta, using an optical high-temperature floating zone furnace. The effects of growth speeds from 5 to 100 mm/h and rotation rates from 5 to 30 rpm on the microstructures of Cr-(9.0-9.8) at.% Ta alloys in pure argon were examined. It was found that a high growth speed of 100 mm/h was necessary for the formation of an aligned microstructure of the Cr-Ta alloy. The influence of DS conditions (growth speeds and rotation rates) and heat-treatments on the hardness at room temperature and tensile properties at room and elevated temperatures (800°C and 1200°C) was investigated in this study.

**Fireside Corrosion Testing of Candidate Superheater
Tube Alloys, Coatings, and Claddings - Phase Iii**

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In Phase I of this project, laboratory experiments were performed on a variety of developmental and commercial tubing alloys and claddings by exposing them to fireside corrosion tests, at 620-730 degrees C that simulated existing and advanced cycle superheaters or reheaters in a coal-fired boiler. Phase II (in situ testing) has exposed samples of 347, RA85H, HR3C, RA253MA, Fe₃Al + 5Cr, 310 modified, NF 709, 690 clad, 671 clad, and 800HT for up to approximately 16,000 hours to the actual operating conditions of a 250-MW, coal-fired boiler. The samples were installed on air-cooled, retractable corrosion probes, installed in the reheater cavity, and controlled to the operating metal temperatures of an existing and advanced-cycle, coal-fired boiler. Samples of each alloy were exposed for 4483, 11,348, and 15,883 hours of operation. The results of the 15,883 hours exposure have been issued in an interim report.

Phase III of this program will expose a variety of developmental and commercial tubing to conditions prototypical of air heaters of advanced cycle power-producing utility plant. This paper will summarize the proposed test conditions for the alloys to be tested.

Computational Modeling of Thermal Expansion and Hydrogen Embrittlement of Iron Aluminides

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In this paper, we first present the status of our computational modeling study of the thermal expansion coefficient of Fe_3Al over a wide range of temperature and evaluate its dependence on selected additives. This will be accomplished by applying an isobaric Monte Carlo technique. The required total energy of the sample will be computed by using a tight-binding (TB) method that allows us to significantly increase the size of the computational data base without reducing the accuracy of the calculations. The parameters of the TB Hamiltonian are fitted to reproduce the band structure obtained by our quantum mechanical full-potential LMTO calculations. The combination of the three methods mentioned above creates an effective approach to the computation of the physical properties of the transition-metal aluminides and it can be extended to alloys with more than two components. At present, we are using a simplified approach for a first-round of results; and as a test of the simplified approach, have obtained excellent agreement with experiment for aluminum. We next present comparative finite element modeling simulations of initial intergranular fracture of two iron aluminides (FA186 and FA189) due to the effect of hydrogen embrittlement. Sequentially coupled stress and mass diffusion analyses are carried out to determine crack-tip stress state and the extent of hydrogen diffusion at the crack tip region, and a proper failure criteria is then adopted to simulate the intergranular fracture. Good agreement between the numerical and experimental results is observed.

Iron-Aluminide Weld Claddings for the Protection of Low NO_x Boiler Tubes

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Recent changes in NO_x emission legislation has led to drastic changes in conventional fossil fuel-fired boiler environments. These environment changes have led to high waterwall wastage rates, due to high-temperature gaseous attack by the reducing atmosphere present in the modified boilers. For years, iron-aluminum based alloys have shown excellent corrosion resistance in both oxidizing and reducing atmospheres. Unfortunately, iron-aluminides are a poor choice for structural components because they possess poor room temperature ductility and they show a drop in strength above 600°C. Instead, iron-aluminides have been studied as weld overlay claddings as they show good weldability at lower aluminum concentrations. Most high-temperature gaseous studies have focused on simple gases that may not be representative of boiler conditions. Therefore, this study was undertaken to react iron-aluminum claddings with various complex gas mixtures, including H₂S, SO₂, CO₂, CO, N₂, and H₂, to create an environment more representative of the boiler. The complex gases covered a wide range of P_{O₂} and P_{S₂}, and contained various levels of moisture. Thermogravimetric studies were combined with Light Optical Microscopy and X-ray Diffraction to characterize the reactions. It was found that highly reducing environments (low P_{O₂}/high P_{S₂}) produced little to no reaction whereas significant reactions could be seen in oxidizing environments (high P_{O₂}/low P_{S₂}).

Design and Development of a Ceramic Hot-Gas Filter for Fossil Energy

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Advanced coal-fueled, power generation systems utilizing pressurized fluidized bed combustion (PFBC) and integrated gasification combined cycle (IGCC) technologies are currently being developed for high-efficiency, low emissions, and low-cost power generation. In spite of the advantages of these promising technologies, the severe operating environment often leads to material degradation and loss of performance in the barrier filters used for particle entrapment. To address this problem a ceramic hot-gas filter is being designed and developed. Due to the testing necessities, a hot-gas candle-filter which integrates the requirements of a cross-flow filter will be fabricated. As a result, a high-purity, stoichiometric mullite, nine inch long, closed-end, candle-filter prototype was fabricated at Oak Ridge National Laboratory (ORNL) using gelcasting technology.

ODS Alloys

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This work focuses on evaluation of oxide dispersion strengthened (ODS) alloys for high-temperature components in advanced fossil systems. ODS alloys offer a unique combination of increased high temperature creep strength as well as excellent oxidation resistance. Matrix compositions being evaluated include FeCr, FeCrAl and Fe₃Al.

Oxide Scale Defects and Damage Processes in Iron-Based Alumina-Formers

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In order to examine the nature of the defects and damage processes controlling the breakdown of protective alumina on iron-based alloys, the effects of thermal cycling on scale morphology and adherence were studied as a function of time at 1200°C for reactive element-containing FeCrAl- and Fe₃Al-based alloys. Damage was characterized by use of scanning and transmission electron microscopy to compare oxide-metal cross sections from specimens that were thermally cycled to those that were isothermally exposed for similar times at temperature. Correlations between damage structures and gravimetric behavior were also made. Surprisingly, few differences in scale and metal-oxide interfacial morphologies/damage were found between thermally cycled and isothermally exposed specimens. The significance of these observations is discussed in terms of proposed models for damage accumulation and alumina scale failure.

Evaluation Of Iron-Aluminide Coatings For High-Temperature Corrosion Protection

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This work comprises part of an effort focused on evaluation of metallic coatings for high-temperature corrosion resistance. The ultimate goal is to identify candidate material systems for significantly extending corrosion-limited lifetimes of high-temperature components in advanced fossil systems. The general approach is based on matching an appropriate synthesis technique (developed elsewhere) with the composition and microstructure required for fossil environments associated with Vision 21 concept technologies. It involves coordination with the appropriate coating efforts sponsored by the Advanced Research and Technology Development Program as well as by others.

Given the excellent high-temperature oxidation-sulfidation resistance of iron aluminides in many prototypic fossil environments, initial work has focused on an examination of iron-aluminum coatings on steel substrates as prepared by weld overlay, chemical vapor deposition (CVD), and thermal spray processes. Overlay and CVD coatings have been prepared at ORNL; spray coatings have been produced by conventional plasma spraying at ORNL and by high-velocity oxy-fuel (HVOF) deposition at Idaho National Engineering and Environmental Laboratory (INEEL). As part of this effort, two approaches to aluminizing steel substrates to form protective iron-aluminide surface layers are being examined. One involves overlays using aluminum rods as the feedstock and the other is by CVD. Preliminary characterization of coatings involved relatively simple high-temperature oxidation exposures, which were found to be sufficient for first-stage evaluation of the protectiveness afforded by the various coatings to the steel substrates. Good resistance was obtained when aluminum concentrations in the coating were uniform and exceeded ~18 at.% without substantial surface cracking. This was problematical for a number of the coatings evaluated to date.

Corrosion Testing of Advanced Materials in Pilot-Scale Coal-Fired Power Systems

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Structural and functional materials used in solid- and liquid-fueled energy systems are subject to gas- and condensed-phase corrosion, and erosion by entrained particles. The material temperature and composition of the corrodents determine the corrosion rates, while gas flow conditions and particle aerodynamic diameters determine erosion rates for a given material. Corrodent composition depends on the composition of the fuel, the temperature of the material, and the size range of the particles being deposited. It is difficult to simulate under controlled laboratory conditions all of the possible corrosion and erosion mechanisms to which a material may be exposed in an energy system. Therefore, the University of North Dakota Energy & Environmental Research Center (EERC) and the US Department of Energy (DOE) National Energy Technology Laboratory (NETL) are working with Oak Ridge National Laboratory to provide materials scientists with no-cost opportunities to expose materials in pilot-scale systems to conditions of corrosion and erosion similar to those in occurring in commercial power systems.

The EERC has two pilot-scale solid-fuel systems available for exposure of materials coupons. The Slagging Furnace System (SFS) was built under the DOE Combustion 2000 program as a testing facility for advanced heat exchanger subsystems. It is a 2.5 MMBtu/hr solid-fuel combustion system with exit temperatures of 2700 to 2900F to assure that the ash in the main combustor is molten and flowing. Downstream of the combustor is a quench zone that injects recirculated flue gas to rapidly drop the gas temperature from 2700F to 1850F prior to entering a convective air heater. Sample coupons may be exposed in the system either within the slagging zone or near the convective air heater. In addition, a pilot-scale entrained bed gasifier system known as the Transport Reactor Development Unit (TRDU) is available. Also operating at approximately 2.5 MMBtu/hr, it is a pressurized unit built to simulate the Kellogg entrained bed gasifier in use at the Southern Company Services Wilsonville facility, but at 1/10 of the firing rate. At the exit of the unit is a large candle filter vessel typically operated at approximately 1000F in which coupons of materials can be inserted to test their resistance to gasifier ash and gas corrosion. The system also has ports for testing of hydrogen separation membranes that are suitably contained in a pressure housing.

In addition, NETL is operating the Combustion and Environmental Research Facility (CERF). In recent years, the 0.5 MMBtu/hr CERF has served as a host for exposure of over 60 ceramic and alloy samples at ambient pressure as well as at 200 psig (for tubes). Samples have been inserted in five locations covering 1700-2600F, with exposures exceeding 1000 hours. In the present program, the higher priority metals are to be tested at 1500-1600 F in one CERF location and near 1800-2000F at other locations to compare results with those from the EERC tests.

Influence of Processing on Microstructure and Properties of Iron Aluminides and Coatings

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Oxide dispersion strengthening has been investigated as a method of improving the creep properties of alloys based on Fe₃Al. Reaction synthesis of the intermetallic from elemental powders has been shown to result in a fine dispersion of oxide particles that increase the time to rupture at 650°C by as much as an order of magnitude compared to conventionally processed material of similar composition. Mechanical alloying to introduce a rare earth oxide has been employed to improve the creep properties at temperatures up to 1000°C. With proper thermomechanical processing, either of the oxide dispersion strengthened materials exhibits secondary recrystallization to a very coarse grain size, further improving the creep resistance compared to conventional material. Steady state creep rates, transmission electron microscopy, and deformation to failure in creep will be discussed for these materials and compared to existing models for creep behavior of oxide dispersion strengthened materials.

Work has begun on developing iron aluminide coatings for resistance to environmental degradation at high temperatures. The influence of process parameters on the microstructure and residual stress of coatings based on Fe₃Al deposited using conventional plasma spray methods and high velocity oxygen fuel deposition are being investigated. In general, coatings deposited using plasma spray techniques are in tension after processing and exhibit poor adhesion. Coatings deposited using high velocity oxygen fuel methods are in residual compression due to the peening effect of impact from solid powder particles at velocities up to 700m/s. These coatings exhibit much improved adhesion.

Corrosion Performance Of Structural Alloys In Coal-Combustion Environments*

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Conceptual designs of advanced coal-fired combustion systems require high-temperature furnaces and heat transfer surfaces that operate at temperatures much higher than those prevalent in current coal-fired power plants. The combination of elevated temperatures and hostile combustion environments necessitates the development and application of ceramic materials in these designs. However, downstream of the combustion zone, a transition from ceramic to metallic materials will be required and the metallic components will experience much more elevated temperatures than those in current combustion systems. Furthermore, they will be subjected to combustion environments in which the deposit and gas chemistries could be different from those in current boiler systems. The objectives of the present program are to (a) evaluate in laboratory experiments the corrosion behavior of candidate metallic materials in simulated combustion environments and (b) evaluate the corrosion performance of the metallic materials in a state-of-the-art, 0.5 MBtu/h pilot-scale combustion and environmental research facility (CERF) designed to achieve similarity with full-scale utility and industrial boilers. Metallic alloys such as Alloy 800, 253 MA, 214, 625, 556, 617, 188, Alloy X, Fe aluminide, and MA 956 have been exposed in the convective section of CERF at 900-1000°C. Results will be presented on posttest examinations of the exposed specimens from the standpoint of scaling type and thickness, internal penetration of the alloy, microstructural characteristics, and overall corrosion performance.

**Development of Intermetallic-Reinforced and Oxide-Dispersion
Ductilized Cr Alloys for Aggressive High-Temperature Environments**

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A new family of structural Cr alloys based on Cr-(6-10)Ta (at.%) is under development for use in oxidizing and aggressive hot corrosion environments at 900-1300°C. The microstructures of these alloys consist of a Cr solid solution matrix reinforced with the intermetallic Cr₂Ta Laves phase as a dispersed second phase particle or in a lamellar Cr solid solution-Cr₂Ta eutectic structure. Substantial progress has been made in developing attractive high-temperature tensile strength, creep resistance, and oxidation resistance through control of alloy composition and structural features. However, room-temperature fracture toughness remains the key concern for development. Three approaches for improved toughness are under investigation: directional solidification, microalloying/microstructure control, and interstitial nitrogen gettering [1] via spinel-based oxide dispersions. The spinel-based oxide dispersion approach shows particular promise and has produced room-temperature tensile ductilities in excess of 10% and fracture toughnesses in excess of 20 MPa√m for unalloyed Cr. Results of mechanical property studies will be presented for both Cr and Cr-Ta based alloys along with results of initial corrosion screening evaluations which indicate excellent resistance in molten salt and slag environments.

[1] D.M. Scruggs, L.H. Van Vlack, W.M. Spurgeon, *J. Amer. Ceram. Soc.*, 51, 9, pp. 473-481 (1968).

Commercial Process for the Production of Silicon Carbide Fibrils

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Phase I of this project demonstrated a new technology for silicon carbide fibril growth that would remove some of the previous impediments to the scale-up to a commercial fibril process. The microwave energy approach was designed to heat only the fibril growth balls, reducing the MTS reaction gas quantities needed to feed the fibril growth process. The continuation of this process development can significantly reduce the fibril growth time and the consumption of expensive raw material gases; therefore, decreasing the future commercial price of the fibril product. The previous Carborundum work concluded with a fibril growth rate of approximately 0.17 millimeters per hour. The Phase I microwave growth process experiments resulted in 0.75 millimeters per hour growth rate. Therefore, the new technology achieved a factor of five increase in growth rate, with minimal optimization work. The near stoichiometric use of raw materials and the increase in fibril growth rate, makes it feasible to attain a volume production price for fibrils of less than \$300 per pound, using the microwave process.

Phase II (FY 2000) investigates growth process parameters and optimization of those parameters. A pilot line microwave furnace and reaction gas control equipment will be designed and fabricated to provide more accurate process operation and data acquisition functions. Experimental work will optimize the fibril growth process in the pilot equipment. Materials analysis of the fibril product with electron microscopy and x-ray diffraction will be used to characterize and improve the silicon carbide fibril product, during the pilot line development. Oak Ridge National Laboratory's capabilities will be used to evaluate mechanical and thermal stability properties of the fibrils. Phase II will conclude with a reasonable definition of the future production process, an approximate specification of the silicon carbide fibril product, and an estimate of the volume fibril price.

Slag - Refractory Interactions: Year +1

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This year's research FOCUSED on efforts to characterize and understand slag component interactions with the refractories used in coal gasifiers. It is anticipated that once these interactions are understood, it might be possible to find a means of controlling, i.e., limiting, the slag-refractory interactions and extending the refractory lifetime.

Last year we developed a laboratory test that simulated commercial coal-gasifier environments, the modified cup-tests. We establish a set of operating test temperatures, times, and gas atmosphere that resulted in slag-refractory interactions that could account for approximately 70 to 80% of the commercial gasifier chamber refractory losses.

This year cup-tests were run with a variety of slag components to determine if it were possible to determine which elements within the gasifier slags were causing or influencing the refractory losses. Individual slag components (Si, Ca, Fe, and C) and combinations of these elements were laboratory tested and the resulting slag-refractory interactions examined for (i) refractory reaction: chemical and morphological, (ii) phase change, (iii) slag penetration, and (iv) refractory solubility. In addition, artificial coal slag, (similar composition to Ill. No.6 coal) and bottom slag from a commercial gasifier were tested under identical conditions.

Results suggest that the principal component of coal slag, SiO_2 , has little effect on the refractory. SiO_2 does however act a carrier for the more reactive slag components and will react with and dissolve the refractory binder components producing a more reactive slag solution. When SiO_2 is combined with other slag components, its viscosity decreases and it rapidly infiltrates into and through the 85% porous high chrome-alumina refractories. The SiO_2 surface tension is sufficient low that the slag runs into and fills small voids but flows through large cavities. Calcia (CaO) and iron-oxide (FeO), in combination with SiO_2 , readily react with and dissolve the chrome refractory and produce low melting eutectics. Calca and silica form a low viscosity solution that easily flows into the refractory. Iron-oxide reacts with chrome at the slag-refractory interface forming a semi-solid spinel phase. Variation in the slag chromium concentration is noted as the slag infused into the refractory. At this point it has not been determined if the higher chromium concentration in the slag with infusion depth is due to (i) changes in the refractory solubility with the changing slag composition as the slag dissolves the refractory and refractory binder elements, and/or (ii) the slag at depth having a greater time of contact with the refractory and thus greater time to dissolve the refractory.

Carbon acts to reduce both the iron oxide and chromium oxide to their metallic states. The formation of metallic iron reduces the formation of the iron-chromium spinel phase and thus offers a possible means of controlling refractory loss.

Corrosion-Resistant Silicon-Based Composites

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Silicon carbide-based materials in the form of sintered SiC, siliconized SiC, or SiC-matrix composites are being examined for use in components such as heat exchangers or hot-gas filters for industrial waste incinerators and advanced fossil- or biomass-fueled power systems. Silicon-based ceramics are typically protected by a slow-growing silica surface scale that limits oxygen diffusion and thus prevents further attack of the substrate. Unfortunately, these SiO₂ scales are susceptible to volatilization by high temperature reactions with water vapor and fluxing by hot corrosion in the presence of alkali salt deposits, such as molten Na₂SO₄. The long-term durability of Si-based ceramic components is thus limited, necessitating the use of protective coatings or the development of materials with improved stability in these harsh environments.

In order to utilize the attractive properties of SiC, systems are being developed that combine oxide and non-oxide ceramics to take advantage of the properties of both families of materials. For example, oxide ceramics coatings are being deposited on SiC and silicon nitride ceramics to protect the bulk materials from corrosion. The oxide coatings commonly called "environmental barrier coatings or EBCs, however, do not completely prevent oxygen diffusion and thus a silica layer is formed between the substrate and protective oxide coating. It is believed that the silica layer will continue to grow with time, albeit very slowly, and eventually cause the protective coatings to fail and spall during thermal cycling.

One solution to this is the development of Si-based coatings and/or matrices that form protective oxides other than silica. It is hypothesized that composite coatings of SiC and aluminum-containing compounds such, as aluminum nitride would form aluminosilicate surface layers upon oxidation. The composition would be optimized to produce mullite, which is chemically and mechanically stable in contact with SiC. The SiC composite coatings would be deposited employing CVD techniques thus could be used as a surface layer, as the matrix, or as a bond coat. Other possible compositions include SiC and Si₃N₄ with additions of hafnium, zirconium, and other metals that would form silicates that are compatible with SiC-based materials. The deposition of SiC and Si₃N₄ composite coatings is being pursued. Thermochemical analysis of the deposition of these composite coatings has been conducted to determine deposition "windows". A furnace has been modified to permit the introduction of the necessary reactants. Initial experiments involving the introduction of aluminum-containing compounds to SiC are being conducted.

Another approach to improving the environmental stability of these materials is to not simply apply a surface layer, but to substitute an oxide material for a portion of the matrix. In the preferred embodiment, the oxide is used as the final portion of the matrix, the material nearest to the surfaces and most likely to be exposed to an external atmosphere. A skeletal structure of SiC fibers, interface coating, and SiC matrix is

formed but not fully densified. The open porosity is then filled with an oxide that is thermochemically and thermomechanically compatible with the bulk material. This approach is similar in many ways to the silicon melt infiltration process. The process overcomes some of the concerns associated with thin external coatings, although a final seal coating may be necessary to completely close surface porosity. Oxides such as mullite, zircon, and select phosphates are suitable candidates. Chemical vapor deposition has been used to infiltrate porous substrates with oxides; however, the process is very slow. Alternate techniques such as sol gel and slurry impregnation are better suited for infiltration of the large pores with oxide ceramics and are thus being explored.

Initially, the impregnation of SiC composites with mullite is being examined. Variations in powder particle size, infiltration technique, and processing conditions are being investigated. Early efforts are focusing on uniformity of infiltration and corrosion resistance. Once these factors are optimized for mullite, other oxides will be examined, and processing conditions varied for maximum retained strength.

Metallic Filters for Hot-Gas Cleaning

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Hot gas cleanup is one of the key technological barriers remaining in the development of advanced coal-fired power cycles. The successful development of such high efficiency, low emission power plant concepts is premised on efficient removal of fine particles and gaseous contaminants from high temperature, high pressure combustion gas streams. Despite research and development over the last two decades, the problems of hot gas cleanup have yet to be resolved. Recent analysis suggests that the metallic candle filter is a more promising approach to hot gas cleanup than the current ceramic filters. A unique spherical powder processing and sintering technique is being developed to fabricate metallic filters having uniform, closely controlled porosity. A Ni-based superalloy, Haynes 214, was selected for initial trials of this processing technique based on its reported ability for stable alumina scale formation and retention of useful strength beyond the 850C requirement of advanced power applications. High pressure gas atomized powder samples of Haynes 214-alloy were tap densified and sintered to densities ranging from 64% to 74% and ambient temperature transverse rupture strengths from 270 MPa to 613 MPa, respectively. Microstructural analysis revealed the sintering conditions necessary to produce open permeable pore networks and sufficient interparticle bonding. Permeability and bubble point measurements indicated the initial filter performance characteristics of the sintered samples. The corrosion resistance of these filter samples and a complete collection of alloy alternatives remains to be evaluated under simulated gaseous combustion environments to determine the suitability of this filter structure and to allow improved alloy selection.

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