High Temperature Materials

by Karl E. Spear, Steve Visco, Eric J. Wuchina, and Eric D. Wachsman

The interdisciplinary nature of ECS is uniquely reflected within the High Temperature Materials (HTM) Division. Here, scientists and engineers are concerned with the chemical and physical characterization of materials, the kinetics of reactions, the thermodynamic properties and phase equilibria of systems, the development of new processing methods, and ultimately, the use of materials in advanced technology applications at high temperatures. The mission of the HTM Division is to stimulate education, research, publication, and exchange of information related to both the science and technology of high temperature materials, which include ceramics, metals, alloys, and composites. While seeking to fulfill its mission, a continuing goal of the Division is to help ensure the development of new materials and processes to overcome the limitations that currently hold back advances in technology. These advances include more efficient and cleaner energy sources and storage systems; smaller and more reliable electronic, magnetic, optical, and mechanical devices; a wider variety of technologically useful chemical sensors and membranes; lightweight, corrosion-resistant structural materials for use at elevated temperatures in extreme environments; and economic methods for recycling and safely disposing of our waste materials.

What is High Temperature?

A definition of high temperature can he confusing. One often used definition in materials science and technology is that it is a temperature equal to, or greater than, about two-thirds of the melting point of a solid. Another definition, attributed to Leo Brewer, is that high temperatures are those at which extrapolations of a material's properties, kinetics, and chemical behavior from near ambient temperatures are no longer valid. For example, chemical reactions not favorable at room temperature may become important at high temperatures—thermodynamic properties rather than kinetics tend to determine the high temperature reactivity of a material. Vaporization processes and species become increasingly important at high temperatures. Unusual compounds and vapor species, which do not conform to the familiar oxidation states of the elements, may form. For example, in the vaporization of Al_2O_3(s), common high temperature gas species can include Al_2O, AlO, and AlO_2. The complexity of the vapor phase also increases with temperature; BeO(s) vapor species include not only the elemental vapors, but at high temperatures, also significant $(BeO)_n$ species, with $n = 1$ to 6. While the vaporization of BeO(s) in air to the elements is suppressed by the oxygen, the $(BeO)_n$ vapor pressures are independent of air, and can produce much larger active corrosion rates than those calculated using only the elemental gas species. With increasing temperatures, ordered defect structures become disordered, and solid solution ranges increase significantly. For example, stoichiometric solids such as $MgAl_2O_4$ may develop significant composition ranges at high temperatures. Physical properties of materials that correlate with the above high temperature chemical behavior are also unpredictable from extrapolations of low temperature properties.

Examples of High Temperature Activities and Materials

High temperature materials provide the basis for a wide variety of technology areas, including energy, electronic, photonic, and chemical applications. While some applications involve the use of these materials at high temperatures, others require materials processed at high temperatures for room temperature uses. In electrochemistry, the interaction of these materials with each other, the atmosphere, and the movement of electrons are of high importance. The high value of a cross-cutting technology such as high temperature materials to a wide variety of technical arenas is reflected by the number of science and engineering disciplines involved in the study of processing and properties of these materials, including ceramic science, chemistry, chemical engineering, electrical engineering, mechanical engineering, metallurgy, and physics. The diversity of interests ranges from experimental observations to predicting behavior, from scientific principles to engineering design, from atomic scale models to performance while in use. A few examples of the diversity of high temperature materials and applications are summarized below.

High Temperature Materials Processing. High temperature materials of interest include not only advanced alloys, but also oxide and non-oxide ceramics and various composite materials. In addition to the chemical and physical properties that make a material important for technology, the ability to synthesize the material in physical forms ranging from powders to thin films to bulk pieces of varying macroscopic sizes and shapes is crucial to their applications. Particle size, grain size, surface structure, chemical purity, crystalline perfection, and degree of crystallinity and homogeneity are all important parameters that may critically influence the end-use properties of a material. The ability to tailor-make an engineered material to within precise specifications requires an enhanced scientific understanding of mechanistic processes that convert starting materials to end product. In many cases this involves high temperature processes, such as sintering for particle densification, or chemical vapor deposition for film growth. The resulting material or device may then utilize frozen-in chemistry and microstructure for operation at room temperature, or for certain devices such as fuel cells operating at high temperature.

High Temperature Fuel Cells. International concerns regarding the emission of greenhouse gases and the trend toward distributed power generation are of current interest to the technical community. According to the most recent U.S. Department of Energy reports, an extensive expansion of installed generating capacity will be required to meet projected electricity demand. U.S. electricity generating capacity is expected to grow from 920 GW in 2003 to 1186 GW in 2030. Worldwide installed electricity generating capacity is expected to grow from 3315 GW in 2002 to 5495 GW in 2025. Clearly, the utility market will respond to the increased demand. The important question is how this demand can be satisfied without simultaneously increasing greenhouse gases and other harmful emissions. Among the various fuel cell technologies, solid oxide fuel cells (SOFCs) and molten carbonate fuel cells (MCFCs) are among the best suited for distributed power generation due to their high system efficiency and ability to reform natural gas internally.

SOFC configurations, as illustrated in Fig. 1a and b, are an example of a complex electrochemical system with challenging high temperature materials problems. The electrolyte must conduct ions (such as O^{2-}), but not electrons, while the electrodes must conduct the electrons generated by the electrode reactions. In addition, the tubes in structural components must be gastight and mechanically stable at high temperatures. This requires minimizing thermal expansion differences among the components, and developing gastight seals for the high temperature use. Developing the technology for producing components that meet these stringent property requirements requires processing schemes that produce specific types of micro- and macrostructures. In addition, the composite components must be chemically compatible with each other and with the fuel. These major high temperature materials challenges appear overwhelming, but they have been met; and improved materials and processes are continually being developed.

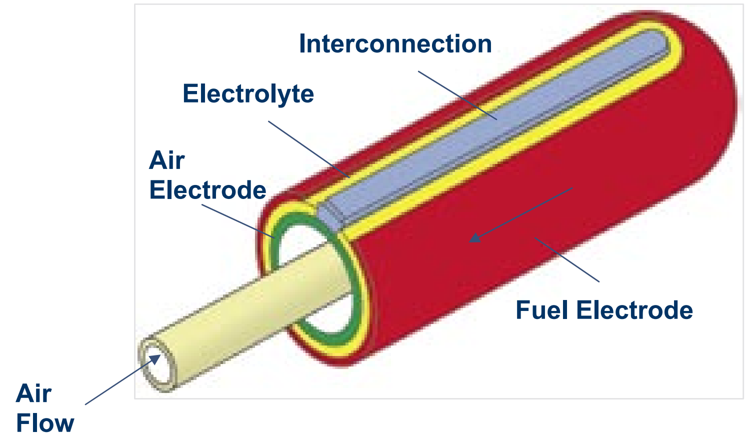

Fig. 1a. *Schematic diagram of a state-of-the-art air electrode support (AES) cell for SOFCs. The porous air electrode tube is doped $LaMnO_3$ [2.2 mm thick, extrusion sintered]; the electrolyte is $ZrO_2(Y_2O_3)$ [40 μm, electrochemical vapor deposited]; the interconnection is doped $LaCrO_3$ [85 μm, plasma sprayed]; and the fuel electrode is $NiZrO_2$ (Y_2O_3) [100 μm, slurry spray-electrochemical vapor deposited].*

Fig. 1b. *Schematic diagram of a SOFC bundle configuration. (Fig. 1a and b courtesy of Siemens Westinghouse Power Generation.)*

Recent advances in materials selection and microstructure, combined with fabrication of electrode-supported thin-electrolyte planar geometries, has resulted in tremendous performance gains. Current advanced planar SOFCs have demonstrated ~2 W/cm² at the cell level, at 700°C. These power densities are greater than previous generation cells at 1000°C, thus, providing the opportunity to utilize less expensive metal interconnects. However, the use of metal interconnects brings with it new challenges in high temperature corrosion prevention.

High Temperature Corrosion. In addition to oxide ceramics, which include not only the SOFC materials along with new sensors and high temperature superconducting materials, silicon-based ceramics such as SiC, Si_3N_4, and sialons along with other borides, carbides, nitrides, silicides, and diamond and diamond-like materials are now common high temperature materials of scientific and technological interest in both bulk and coating configurations. SiC and Si_3N_4 have properties of value for advanced microelectronic applications as well as for use as lightweight structural components at high temperatures. Single crystal SiC can be used as a high temperature semiconductor, and Si_3N_4 and its oxynitride Si_2N_2O provide excellent insulating coatings in device production. As bulk ceramics, both materials are lightweight and can be used in structural applications at higher temperatures than is possible for metal alloy systems. Also, SiC particles, fibers, and weaves have been used extensively in composite materials developed for lightweight, high temperature structural applications. However, a

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High Temperature Materials

(continued from previous page)

major problem of corrosive oxidation at high temperatures must not only be minimized, but as important, it must be understood so component lifetimes are available for design engineers. At low oxygen partial pressures, these silicon-based materials actively oxidize to SiO(g), but at higher pressures, a protective SiO_2 glassy coating forms on the surfaces of the component, dramatically slowing the oxidation rates. These rates can be predicted reliably. However, complex combustion gases contain active species in addition to oxygen which greatly enhance degradation rates. More recently, the enhanced water vapor corrosion of silicon-based ceramics in hydrocarbon-fuel combustion environments has led to an entirely new research area. The formation of volatile $Si(OH)_4$ in gas-turbine engines for both electricity generation and propulsion applications was not considered a major material degradation mechanism a few years ago. However, the shortened service lives of combustion liners, turbine blades, and vanes has led to the development of environmental barrier coatings (EBCs) to protect the base load-bearing material, either SiC/SiC_f composites or monolithic Si_3N_4. These coatings are tailored to be thermodynamically stable in water vapor at very high combustion temperatures, protecting the structural integrity of the components. Much of this work has focused on celsian-based ($BaO{\bullet}Al_2O_3{\bullet}2SiO_2$) and rare-earth (RE) silicate ($RESiO_5$) coatings.

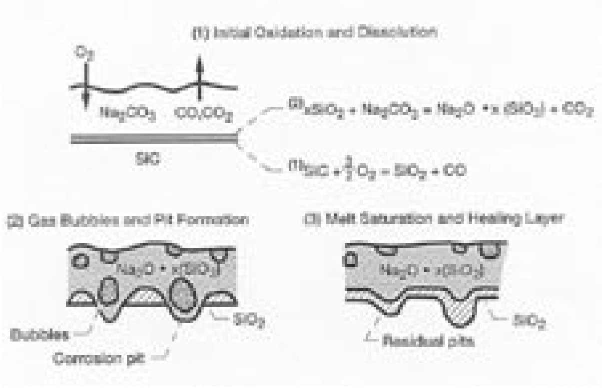

Fig. 2. *Schematic of pitting forming via bubbles in the oxidation of SiC in combustion gasses containing alkali metal salts. (1) Initial stages, (2) intermediate stages, and (3) later stages. (Courtesy of N. Jacobsen and J. Smialek at NASA Glenn Research Center.)*

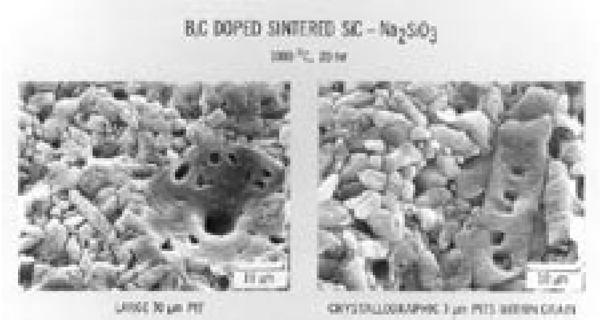

Fig. 3. *Photomicrographs illustrating pit formation during oxidation of sintered SiC in a combustion atmosphere. A mechanism explaining the formation is given in Fig. 2 (Courtesy of N. Jacobsen and J. Smialek at NASA Glenn Research Center.)*

The high temperature oxidation of SiC in combustion atmospheres is of high interest to the technical community. An example of the materials problems encountered in high temperature applications is the effects of alkali amid sulfur impurities in the combustion gases that lead particularly to shortened service life and system failure. Figures 2 and 3 illustrate the effects of alkali (Na) during the oxidation of SiC in a combustion atmosphere. The Na_2CO_3 forming on the surface of the SiC from the combustion gas components reacts with SiO_2 which is produced in the oxidation of SiC. The sodium silicate glass that forms not only releases CO_2, but also eliminates the protective SiO_2 layer which forms in a clean oxygen environment. The high rates of oxidation can then continue, causing a pressure buildup at the SiC interface which produces gas bubbles, as shown schematically in Fig. 2. Figure 2 shows a mechanism that allows a SiO_2-rich layer to form at the SiC interface at longer times, again providing some protection and slowing the rate of oxidation to a point that further bubble formation is eliminated. The effects on the SiC component are shown in the micrographs in Fig. 3.

High temperature materials research in the metals and alloys area is still an extremely important field, and new alloy and composite systems are continually being developed for new applications. The ferrous metallurgy of early days has also broadened to include a broad spectrum of high temperature tungsten, tantalum, titanium, nickel, and NiCrAl-based alloys for various applications such as in high temperature gas turbines.

Brief History of HTM Division

The roots of the High Temperature Materials Division can be traced back to 1921 when it was founded as the Electrothermics Division, the first formalized Division of The Electrochemical Society. Some Society technical committees that merged in 1921 to form the Electrothermics Division were Electrodes, Carbons; Carbides, Abrasives, Refractories; FerroAlloys; and Electrometallurgy. In 1954, in recognition of the importance of high temperature alloys in future technological developments, the Electrothermics Division changed its name to the Electrothermics and Metallurgy Division. However, the broadening diversity of materials and their synthesis and/or applications at high temperatures continued during the next twenty-five years, and were accompanied by a broadening of the membership and activities of the Division. The result was a change in 1982 to the Division's current name, High Temperature Materials. The focus of the Division has expanded significantly from its origins in high temperature materials chemistry and corrosion to encompass high temperature electrochemical systems such as SOFCs, ionic membranes, sensors, and the science and technology of chemical vapor deposition and related processes. The High Temperature Materials Division's activities and interests cut across many scientific and technical disciplines, and serve the needs and interests of Society members in several divisions.

HTM Division Activities

The above-stated mission of the High Temperature Materials Division—to stimulate education, research, publication, and exchange of information related to the science and technology of high temperature materials—has been most actively pursued by sponsoring and cosponsoring international symposia, many of which produce proceedings volumes. The obvious overlap of interests between the HTM Division and those of other ECS Divisions has resulted in many symposia being cosponsored by HTM with other Divisions. Major symposia sponsored or cosponsored by the Division include

Chemical Vapor Deposition. This ongoing series of symposia started in 1967, and has continued with meetings typically held every two to three years. The extended lifetime of this series is a good measure of the ever increasing importance of thin films and coatings in modem technology. A diverse array of topics in CVD including fundamental principles of gas phase and surface chemistry, kinetics and mechanisms, thermochemistry, mass and energy transport, fluid dynamics, and precursor design and synthesis, as well as topics in modeling and experimental verification of CVD processes. These symposia also cover applications in optical materials, semiconductors, superconductors, insulators, and metals. Further topics include dielectrics, ferroelectrics, magnetic materials, nuclear materials, hard coatings, refractories, organic materials, thermal and environmental barrier coatings, as well as multilayers, and solid lubricants.

Solid Oxide Fuel Cells and Molten Carbonate Fuel Cells. Increasing worldwide interest in fuel cells for clean and efficient electrochemical power generation has resulted in a large international research and development effort. The HTM Division has provided a focal point for the technical community to present and discuss its findings by organizing successful symposia on both SOFCs and MCFCs. The highly successful biennial symposia on high temperature SOFCs developed a particularly strong international following, with meetings in this series also held in Greece, Japan, and Germany. Topics in the area of solid-state ionic devices include modeling and characterization of defect equilibria, theories for ionic and electronic transport, studies of interfacial and electrocatalytic properties of ion conducting ceramics, and novel synthesis and processing of thin films and membranes.

High Temperature Corrosion and Materials Chemistry. Extensive work has been carried out since the pioneering work of Carl Wagner to understand and reduce the deleterious effects on materials exposed to harsh environments at high temperatures. The HTM Division remains a focal point for scientists and engineers to discuss new measurements and understanding in this technologically important high temperature field. Measurements and predictions of the high temperature chemistry related to processing, fabrication, behavior, and properties of materials systems in both reactive and nonreactive environments are topics of general interest. Session topics have included fundamental aspects of high temperature oxidation, high temperature corrosion, and other chemical reactions involving inorganic materials at high temperatures. One objective of these symposia is to encourage the development of theoretical models, based on experimental results, which allow the prediction of high temperature reactions and the rates at which they occur. Real-world problems such as alloy and ceramic oxidation, molten salt corrosion, volatilization reactions, and coating durability in complex environments are all addressed in these symposia. These issues are of interest for such diverse applications as power generation, aerospace propulsion, metal halide lamp design, and waste incineration.

Ionic and Mixed Conducting Ceramics. This field has attracted a large body of researchers worldwide and has grown rapidly in the past decade. Topics covered in recent symposia include ionic transport in solid electrolytes, mixed conduction in ceramics, electrocatalytic phenomena, electrochemical processes for hydrocarbon conversion, electrode reactions in solid-state electrochemical cells, batteries and fuel cells involving ceramic components, thin-film ceramic membranes, and applications in ceramic sensors.

Solid-State Ionic Devices. Solid-state electrochemical devices, such as batteries, fuel cells, membranes, and sensors, are critical components of technologically advanced societies in the 21st century and beyond. The development of these devices involves common research themes such as ion transport, interfacial phenomena, and device design and performance, regardless of the class of materials or whether the solid state is amorphous or crystalline. The intent of this international symposia series is to provide a forum for recent advances in solid-state ion conducting materials and the design, fabrication, and performance of devices that utilize them.

Conclusion

As stated previously, it is primarily the ECS High Temperature Materials Division that is concerned with the chemical and physical characterization of materials, the kinetics of reactions, the thermodynamic properties and phase equilibria of systems, the development of new processing methods, and ultimately, the use of materials in advanced technology applications at high temperatures. As more complex and diverse problems are encountered, the mission of the HTM Division becomes increasingly important — to stimulate education, research, publication, and exchange of information related to both the science and technology of high temperature materials. Efforts to fulfill this mission will continue through the Division's major activity of sponsoring and cosponsoring international symposia to promote communication among the interdisciplinary groups investigating high temperature materials. ■

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