Spinel Phase Improves Performance of Lining of Steel-Making Furnace

Ceramic engineers at the University of Missouri-Rolla recently completed a five-year study of the refractory materials that line the two principal processing furnaces used in making steel. The researchers found that the furnace lining materials are more heat- and chemical-resistant when a spinel phase develops inside the lining.

"This phase occurs in high concentrations near the hottest face of the lining and greatly enhances resistance to erosive wear and penetration by unwanted slags and vapor," said Robert E. Moore, professor and chair of the UMR ceramic engineering department and director of the AISI Development Program at UMR. "As a result, the linings behave somewhat like smart materials—materials that sense and respond to external influences."

Moore and his fellow researchers found that the development of the spinel compound within the refractory material is largely responsible for the extended life of the linings.

"These modern composite linings can last up to 10,000 melts," Moore said. "Conventional nongraphite lining materials lasted an average of a few hundred."

The research has been funded by over $700,000 from the American Iron and Steel Institute.

Moore and his colleagues recently received another AISI grant to study ways to improve the lining of huge ladles, which can hold as much as 300 tons of molten steel.

According to Moore, the ladle processing also allows steel companies to better use electric furnaces as well as oxygen convertors during the first phase of steelmaking. Oxygen convectors process the pig iron and iron ore better than electric furnaces, but electric furnaces are less expensive to operate and better for melting scrap. The ladle processing further refines and purifies the molten steel, Moore adds, making it easier to roll into sheets, rods, and plates.

The linings of these ladles are increasingly made of refractory concrete, but concrete has water mixed with it, so the ladles need time to properly dry. This results in a longer shut-down time and less productivity.

Moore and his fellow researchers in the UMR ceramic engineering department have received a five-year, $600,000 AISI grant to study fundamental ways of dewatering or removing the water from the concrete so as to prevent degradation. The researchers are looking into ways of controlling the permeability, or the ease with which steam and water can flow through the micron-size pores of the concrete. If the permeability of the concrete is too high, the concrete will not resist chemical attack. If the permeability is too low, steam pressures may exceed the strength of the concrete, leading to failure during dryout.

Research Center Features Polymer Interfaces and Macromolecular Assemblies

Scientists at IBM's Almaden Research Center (San Jose, California), Stanford University, and University of California-Davis are joining forces at a new federally funded center to study and develop thin film materials for potential use in video displays, lubricants, adhesives, electronic devices, optical systems, sensors, and other high-tech products.

The new center, the Center for Polymer Interfaces and Macromolecular Assemblies (CPIMA), is one of 11 Materials Research Science and Engineering Centers announced by the National Science Foundation (see From Washington department elsewhere in this issue). CPIMA is slated to receive $11.2 million in Federal funding over the next four and a half years, as well as substantial contributions from IBM, Stanford, UC-Davis, and the State of California.

CPIMA is the first NSF materials research center with a private corporation as an equal partner. Industrial involvement in the past had been primarily through industrial affiliates programs.

A major goal of CPIMA is to learn how to create polymer films with specific properties that will enable new technologies, including electronic and optical devices that are smaller and more energy-efficient than current devices. For example, some films as thin as one molecular thick may self assemble to maintain the required molecular alignment of an overlying layer of liquid crystal material used in flat-panel video displays.

CPIMA research will be focused in three interrelated groups:

1. Polymer Design for Enhanced Film Properties: Exploring the physical and chemical properties of new polymers and how these properties change when confined to nearly flat, two-dimensional thin films or interfaces, and how these constrained polymers' properties change in response to external conditions, such as temperature, shear deformation, electric fields, and light. New electroluminescent display materials are among the applications.

2. Ultrathin Mediator Films: Designing ultrathin organic polymer films (less than 50 angstroms thick) that attach to a substrate and mediate the mechanical, optical, and/or electrical properties of a third overlayer and/or the chemical interactions between the upper and lower materials. Applications include microelectronics packaging, lubricants for magnetic hard-disk drives, and computer displays/monitors.

3. Dynamics of Interfacial Processing: Studying the dynamic mechanisms that occur during the processing of ultrathin polymer films and nanocomposites with nanometer-sized metal and/or semiconducting particles embedded within a polymer matrix. Of particular interest are the changes in a material when exposed to high shear stresses, and the relaxation that occurs after such stress is withdrawn. Such information will be vital to the design of new coatings, adhesives, and lubricants. Nanocomposite materials may result in new optoelectronic materials and archival data storage media.

The director of CPIMA is Curtis W. Frank (Stanford), and the co-directors are John F. Rabolt (IBM Almaden), and Pieter Stroeve (UC-Davis).

SBIR Update

EMCORE (Somerset, New Jersey) will use a $750,000 Phase II SBIR award from the U.S. Air Force to develop cluster tool reactors for materials growth on 4 in. and 6 in. diameter compound semiconductor wafers. The compound materials produced will be characterized structurally, optically, and electrically.

Advanced Refractory Technologies, Inc. (ART), (Buffalo, New York) was awarded $65,000 in Phase I SBIR funding by the National Science Foundation to develop thermally conductive fillers for polymers. ART's research focuses on the synthesis and evaluation of A1N powders exhibiting a variety of shapes, sizes, and morphologies. ART was also awarded $620,000 in Phase II SBIR funding by the U.S. Air Force to develop advanced thin film coating for high energy applications. This work continues from efforts completed in the related Phase I program demonstrating that diamond-like nanocomposite (DYLYN™) thin films possess the properties important for protection of insulators used in modern high energy plasma devices.

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Reflections Shed Light on Mechanism of High-Temperature Superconductivity

A subtle difference in the way high-temperature superconductors reflect light when they switch between normal and superconducting states may indicate how these materials superconduct.

Writing in the 24 October 1994 issue of the journal *Physical Review Letters*, a Stanford research team reports measuring such a difference and says that it provides the most direct evidence yet obtained of the nature of the force or forces that bind the current-carrying electrons into pairs, a necessary condition for superconductivity.

The researchers are Stanford physics professor William A. Little, chemistry professor James P. Collman, and postdoctoral fellow Matthew J. Holcomb.

"At a minimum, this observation puts a powerful new constraint on existing theories. A number of theories that are currently popular will have difficulty explaining it," Little said.

The key to understanding the high temperature superconductors is determining the nature of the force or forces that bind the electron pairs together strongly enough to sustain higher temperatures. One hypothesis envisions a magneticlike interaction that arises from electron spin replacing phonons as the binding force. But, magnetic forces should cause a reflectivity shift opposite of that which the researchers observed. Another theory suggests that phonon-bound electron pairs gain additional strength by skipping from one copper-oxygen layer to another. However, this phonon mechanism should have no effect on reflectivity.

According to the scientists, their experimental results provide strong support for a less radical modification to the original BCS theory that explains low-temperature superconductivity, one in which electron excitations supplement phonon forces. Little proposed this mechanism over 30 years ago as part of an effort to design an organic superconductor.

If the Stanford scientists' model is correct, it implies that further increases in critical temperature should be possible. "Theoretically, you can alter the strength of the binding energy by altering the local field in the layers. Nobody knows how to do this in a sensible fashion, but there is no reason to believe that the effect is limited to -150°C. Another factor of two is not unlikely," Little says.

Little and his colleagues have attempted to determine the nature of the binding force in the new class of superconductors by using thermal difference spectroscopy. The technique, developed by Holcomb, allowed them to measure temperature-induced changes in reflectivity as small as one part in 50,000. A special microminiature gas refrigeration system that Little invented allowed them to control the temperature of the material extremely precisely and with very little vibration. In this fashion they were able to measure the way in which $Tl_2Ba_2Ca_2Cu_3O_{10}$ reflects light when its temperature is 5 degrees above and then 5 degrees below the material's critical temperature.

The experiment is based on the argument that the electron pairs resonate at an energy that corresponds to that of the binding force. As a result, the material will absorb light more strongly at this energy level and will reflect more photons at an adjacent level.

The resultant difference in reflectivity is extremely slight, within one part in 500. But the Stanford scientists report that they find such a change in the material's reflectivity while superconducting comparing to its reflectivity in the normal state at about 1.6 eV.

According to the scientists, this reflectivity difference is caused by both phonon distortions in the lattice and an electron excitation created by nonconducting electrons jumping back and forth between oxygen and copper atoms. In these materials, the superconducting electrons move through the oxygen lattice. As a conduction electron passes an oxygen atom, one of the oxygen's nonconducting electrons temporarily jumps to a neighboring copper atom, leaving the oxygen briefly with an excess positive charge before it jumps back. This positive charge attracts the following electron, strengthening the bond between the pair. The energy required for one of these electrons to jump between the oxygen and copper atoms is 1.6 eV.

When the scientists plug this model into the BCS theory, as reformulated in 1960 by Gerasim M. Eliashberg from the Landau Institute in Moscow, to take into account stronger binding forces, they are able to derive reflectivity curves with all the features that they observed experimentally.

A New Family of Polymers Developed for Continuously Flexing Biomedical Devices

Robert S. Ward, president of The Polymer Technology Group, Inc., in Emeryville, California reported at the American Institute of Chemical Engineers' (AIChE's) Annual Meeting advances made using surface-modifying end groups (SMEs) chemically bonded to a base polymer during synthesis. "The

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SME approach is being used to develop a new family of biomedical polymers currently being evaluated for use in long-term, continuously flexing implanted devices, including an electrically-actuated ventricular assist device," he said.

Initially, commercial-grade polymers were used to fabricate a number of implantables currently in clinical use, including vascular grafts, pneumatic ventricular assist devices, and artificial hearts. Recent advances in the technology, Ward said, include the surface modification of these polymers during and after device fabrication.

We have also used the SME approach to enhance a protein-permeable immunoisolation membrane and a hybrid artificial pancreas (HAP)," Ward said. An HAP is a combination of artificial materials and living cells that can release insulin in response to changing glucose levels in the area of the device to approximate normal levels of sugar in the blood. By solvent casting the polymer on a continuous web coater, strong, nonporous, stretchy membranes are created that can be fabricated into sheets or hollow fiber shapes. HAPs can be fabricated by die cutting membranes and bonding to form the implantable devices.

This is good news for those who have insulin dependent (Type 1) diabetes, which is characterized by deficient insulin production and/or release.

Ward said that "these new biomedical polymers do not have permanent pores. The surface of the membrane is remarkably smoother than that of a typical microporous membrane. This is important when considering tissue reaction to the implanted material. Our results demonstrate that this material is readily permeable to both insulin and glucose, but is apparently impermeable to immunoglobulins."

Ward reported that the immuno-isolation membrane developed using SME has proven to be nontoxic and sufficient nutrients pass through the membrane material to support cell growth, and the cells within the material are protected from the host's immune system. Ward's studies demonstrated that tubes fabricated from the nonporous segmented polyurethane not only protect the cells from the host's immune system, but also protect the host from the cells within the membrane.

Chocolate's Physical Properties Retained While Cost and Fat Content Reduced

Engineers at The Pennsylvania State University are researching ways to reduce the cost and fat content of chocolate while retaining its texture and taste.

In a session on food engineering at the American Institute of Chemical Engineers' (AIChE's) Annual Meeting in San Francisco, Greg Ziegler, an associate professor of food science at Penn State, and Brian Fischer, a recent Penn State graduate and now an engineer with Raskas Cheese Products, Shippensburg, Pennsylvania, said that such a chocolate may not be far off.

"Semi-sweet chocolate," Ziegler said, "is basically a concentrated suspension of cocoa and sucrose particles dispersed in a continuous fat phase. The primary component of this fat is cocoa butter, which also happens to be the most expensive ingredient. The key is to minimize the fat content while still retaining chocolate's unique physical properties and flavor."

Up to now, most research has concentrated on the size of cocoa and sugar particles suspended in the fat, which is important for taste purposes. The Penn State study takes this research a step further by designing the particle size distribution to optimize the flow properties of the chocolate.

Flow behavior of chocolate is important in molding and enrobing (for chocolate bars), for proper cookie drop (such as chocolate chips) formation, and in the design of bulk handling systems. The key to this flow behavior is chocolate's viscosity, which is primarily determined by fat content. While the fat content of most chocolates is around 30%, most experts feel lower levels are attainable.

The researchers examined four distinct particle size distributions—narrow unimodal, wide unimodal, bimodal, and control—maintaining a mean particle size, which is important for taste purposes. Viscosity was then measured at four nominal fat contents—25, 28, 31, and 34 percent.

The researchers found that the bimodal particle size distribution resulted in a lower viscosity and higher yield value than the unimodal distributions. More importantly, Fischer noted, "The lower the fat content, the greater the effect." He added that the results were consistent with a physical model of packing efficiency in suspensions.

Ziegler concluded, "Cocoa butter content can be reduced while maintaining nearly identical flow properties, resulting in a cost savings to manufacturers, and perhaps more importantly, reducing the caloric content."

Recently Announced CRADAs

Pacific Northwest Laboratory (Richland, Washington), **Westinghouse Electric Corporation** (Pittsburgh, Pennsylvania), and **Seattle Specialty Ceramics, Inc.** (Woodinville, Washington) will combine efforts to synthesize solid oxide fuel cell materials. Solid oxide fuel cells are being developed for large scale power generation that is highly efficient and results in low NO_x and SO_x emissions.

Fauchet Awarded Guibal-Devillez Prize for Porous Silicon Publication

Philippe M. Fauchet, professor of electrical engineering at the University of Rochester and senior scientist at the University's Laboratory for Laser Energetics, has been awarded the Guibal-Devillez Prize from the Faculté Polytechnique in Belgium.

The prize, named after the two founders of the institute, is given once every four years to the author of a publication signaling a major discovery in applied technology.

Fauchet received the prize for his paper on porous silicon.

Fauchet is studying the material's light-emitting properties and is exploring applications such as solar cells where the material would be used to convert the sun's rays into useful energy. Fauchet is collaborating with engineers at Xerox Corp. and CVD Inc. to improve the material's efficiency. His work on porous silicon is supported by the New York State Energy Research and Development Authority and Rochester Gas & Electric.

Fauchet is a graduate of the Faculté Polytechnique, Brown University, and Stanford University, and taught at Stanford and Princeton before joining the University of Rochester in 1990. He has received several awards, including a Sloan Research Fellowship, an NSF Presidential Young Investigator Award, and an IBM Faculty Development Award.

Fauchet has authored nearly 150 publications and invited papers and presentations and has chaired several conferences and symposia with SPIE, IEEE LEOS, and MRS. He co-chaired the 1993 MRS Fall Meeting.

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MRS Engineers Honored by AIChE

Three MRS members were among the 23 recipients of the 1994 awards of excellence granted by the American Institute of Chemical Engineers (AIChE). **Matthew V. Tirrell** from the Department of Chemical Engineering and Materials Science at the University of Minnesota received the Professional Progress Award for Outstanding Progress in Chemical Engineering; **Julio M. Ottino** from the Chemical Engineering Department in Northwestern University received the Alpha Chi Sigma Award for Chemical Engineering Research; and **Nikolaos A. Peppas** from Purdue University received the Food, Pharmaceutical, and Bioengineering Division Award. AIChE presented the awards during its annual meeting held Nov. 13–18, 1994.

Calvin S. Fuller, co-inventor of the solar cell that made the space program practical, died 28 October 1994 at his home in Vero Beach, Florida. He was 92.

A chemist at AT&T Bell Laboratories for 37 years, he also served as head of synthetic rubber research during World War II in the Office of Rubber Director, and later was a consultant to the Defense Department's Research and Development Board.

With Gerald L. Pearson and Daryl M. Chapin, Fuller invented the first practical device able to convert sunlight into useful electrical power. The device was demonstrated in 1954 by powering a transistor radio at the Bell Labs facility in Murray Hill, and in 1962 solar cells provided the power for AT&T's pioneering Telstar communications satellite.

For their work on the solar cell, Fuller, Pearson, and Chapin shared the John Scott Medal from the City of Philadelphia in 1956, the Wetherill Medal from the Franklin Institute in 1963, and Germany's Krupp Prize and medal in 1981.

A native of Chicago, Fuller joined Bell Labs after receiving his doctorate in physical chemistry from the University of Chicago in 1929. His early research was on organic insulating materials, plastics, and synthetic rubber, and in 1948 he began concentrating on developing semiconductor devices.

Among his 33 patents is a technique of infusing impurities into the surface of a silicon wafer, and this discovery led to the solar cell.

He was a member of Phi Beta Kappa, Sigma Xi, the American Association for the Advancement of Science, and the American Chemical Society.

Fullerenes Used to Pattern SiC

The first practical applications of "buckyballs" in the manufacture of silicon carbide microchips, electromechanical devices and sensors appear possible as a result of research at the Lawrence Livermore National Laboratory.

Buckyballs are soccerball-shaped carbon molecules more formally known as buckminsterfullerenes.

Livermore researchers Mehdi Balooch and Alex Hamza of the Laboratory's Chemistry and Materials Science Department found that when they bombarded heated silicon wafers with a stream of buckyballs, the round carbon molecules open up to form silicon carbide in intricate, controllable patterns.

"This technology...may allow us to do many things with silicon carbide that we now do with silicon," Hamza said.

"Silicon carbide is a very promising material for semiconducting application," Hamza added. "Prototype devices have been made, but it's extremely difficult to work with. The material is so inert, it's difficult to etch."

The Livermore engineers' method bypasses this difficulty. "Our technique for patterning chips means that we don't need etching," Balooch said.

When buckyballs encounter a heated silicon surface, Balooch said, "the molecules open up like tulips. They cover the surface, forming silicon carbide layers."

But buckyballs do not react with silicon dioxide. The researchers took advantage of this property to pattern chips into regions covered by silicon alongside areas of silicon dioxide, using standard lithographic techniques. Then they heated the wafers to 1200 K inside a vacuum chamber and exposed them to a stream of buckyballs.

"The buckyballs stick to the silicon and bounce back from the oxide," Hamza said. "After exposure to hydrofluoric acid, the oxide dissolves and what remains is a silicon carbide microstructure."

The Livermore scientists envision multiple applications for their technology, including microelectromechanical devices such as pressure sensors to control auto fuel injection, flameout detectors in aircraft engines, accelerometers used in auto airbag systems, and tiny engine parts built onto microchips.

Hamza and Balooch's results were published in the October 1 issue of *Surface Science*. Mehran Moalem of U.C. Berkeley is a co-author of the article. □

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