Crystalline Zinc Ferrite Synthesized Near Room Temperature

Researchers headed by Michio Inagaki at Hokkaido University, Japan, have synthesized well-crystallized zinc ferrite powder from a mixed-metal solution of $ZnCl_2$ and $FeCl_2$ near room temperature. A single phase of zinc ferrite was formed through the so-called green-rust phase containing Fe^{2+}, Fe^{3+}, Zn^{2-}, OH^-, and Cl^- within a temperature range of 30–60°C, after aging for more than 2 h. Below 25°C, the green-rust phase, which can then be crystallized to spinel only by heating above 400°C, transformed to an amorphous phase upon aging. Iron-zinc ceramic powders for manufacturing magnetic heads can be made more cheaply using this low-temperature method. An article on this research was published in the *Journal of Materials Chemistry*, Vol. 3, 1993.

A simple low-temperature process for synthesizing ceramics, particularly electronic and magnetic ceramics, has been widely sought because of the need to save energy and resources. There are two conventional ways of making iron-zinc oxide ceramics: a solid-state reaction that requires temperatures above 900°C and a sol-gel method that requires less heat. In the conventional solid-state reaction method, the material must be repeatedly heated and pulverized to ensure complete mixing of the iron and zinc. Since heating must take place at temperatures above 900°C, the entire process consumes large amounts of energy. The sol-gel method involves lower temperatures but still must be conducted at 400°C. The sol-gel process is also more complicated because the zinc and iron hydroxides formed from the respective starting materials react with each other to form zinc ferrite.

For low-temperature synthesis, the selection of an appropriate phase, which would be an intermediate to the final product, is important. The researchers looked at the green-rust phase as an intermediate in order to synthesize crystalline zinc ferrite powders. In the new method, zinc chloride and iron chloride are dissolved in water, mixed in ammonia or hydrazine, then aged under agitation. This process is believed to involve the oxidation of Fe^{2+} ions to Fe^{3+} with air. When the solution is continually agitated while kept between 30 and 60°C, a fine powder of crystalline zinc ferrite precipitates out and collects at the bottom of the reaction vessel. The ceramic particles range between 0.1 and 0.5 μm in diameter.

Preliminary experiments to synthesize cobalt and nickel ferrites using the new method suggest success. The powder can also be sintered in a mold to produce useful structural materials.

F.S. Myers

Ultrafine Magnetic Structure Revealed in Co-Cr Alloy

Japan's Nippon Telegraph and Telephone Corporation (NTT) says that it has discovered a magnetic structure finer than crystal grains. Previously, grain boundaries were believed to be the smallest microstructural site at which magnetic decoupling could occur, and thus the smallest possible magnetic unit for storing information in Co-Cr-based recording media. According to researchers Koji Takei, Jun-ichi Suzuki, Yasushi Maeda, and Yukio Morji, experiments have revealed an ultrafine magnetic structure in Co-Cr alloy thin films with a periodicity of about 8 nm, which is about 10 times smaller than the grain diameter. This research will be published in a paper entitled "Micromagnetic Domain Observations of Co-Cr Films by Neutron Scattering" in *IEEE Transactions on Magnetics*, November 1994.

Until recently, magnetic recording media, such as videotapes, were generally based on a polymer coating impregnated with a powder of fine magnetic particles. Computer hard disks and other applications which require higher density recording, however, now store information in a continuous metal-alloy thin-film coating. The recording density possible with such media has increased more than 10-fold over the past decade, resulting in disks that can store up to 30 megabits of information per square centimeter. If this trend continues, recording densities of around 1–2 gigabits per square centimeter can be expected within a few years. To achieve such recording densities, however, researchers believe that it will be necessary to create within the thin film a magnetic structure which simulates a distribution of ultrafine magnetic particles.

Since cobalt is magnetic and chromium is not magnetic, the distribution of these elements has a strong effect on the local magnetic properties of a Co-Cr alloy thin film. In order to investigate the local compositional distribution, NTT researchers chemically etched a series of sputter-deposited Co-Cr films to preferentially dissolve the cobalt. Electron microscope study then revealed that a fine flowerlike pattern had appeared within the grains of films deposited at elevated substrate temperatures (200°C). The researchers surmised that the distribution of the cobalt and chromium within the grains was inhomogeneous and proposed that this would create magnetic features smaller than the crystal grains. In order to confirm the presence of such compositional inhomogeneities, nuclear magnetic resonance was used to investigate the distribution of the Co in the films. It was found that films with the flowerlike structure absorbed greater amounts of electromagnetic radiation at higher frequency than those with no flowerlike structure. From this, they were able to confirm that films with the flower structure contained regions with high concentrations of cobalt (a "cobalt-enriched component").

To test whether such cobalt-enriched regions did indeed affect the magnetic microstructure, the researchers used a small-angle neutron scattering apparatus at a reactor of the Japan Atomic Energy Research Institute (JAERI) to irradiate a sample of Co-Cr with a neutron beam. The scale of the magnetic structure was then deduced from how the neutrons were scattered by the cobalt-enriched (highly magnetic) component. The experiment confirmed the presence of an ultrafine magnetic structure with a periodicity of about 8 nm in films with the flower structure. This figure of 8 nm matched the spacing of the Co-enriched stripes (or petals in the flower structure) of the chemically etched patterns observed in the electron microscope. Hence, it was confirmed that Co-Cr films which exhibit a flowerlike in-grain compositional distribution sustain magnetic features an order of

Recently Announced CRADAs

Performance Alloys Inc. (Secaucus, New Jersey) and the Argonne National Laboratory (Argonne, Illinois) will seek better ways to make high-temperature superconducting solids from powders. Their one-year, $100,000 project aims to process yttrium-barium-copper-oxide (YBCO) by self-propagating, high-temperature synthesis. Resulting specimens are to be evaluated for their density, purity, superconducting properties, and mechanical properties.

Ceradyne, Inc. (Costa Mesa, California) and the Oak Ridge Y-12 Plant (Oak Ridge,Tennessee) will explore ways to reduce costs of machining technical ceramics to very exacting manufacturing requirements without damaging the material. Their CRADA is a three-year, three-phase $1.2 million agreement.

magnitude smaller than the crystal grains.

With current recording techniques, this magnetic microstructure could lead to recording densities of approximately 10 gigabits per square centimeter. A 2.5-inch disk would then have data storage capacity about 100 times greater than the capacity of existing magnetooptical disks, which are ultimately limited by light wavelength restrictions. If, however, data could be recorded with the same periodicity as the newly discovered magnetic features, it would be possible to achieve a recording density of 1 trillion bits per square centimeter, allowing a single 2.5-inch disk to store approximately 1,000 years worth of the information contained in daily newspapers.

F.S. MYERS

Ti-Ni-Cu High-Performance Shape-Memory Alloy Produced by Rapid Quenching

A titanium-nickel-copper-based high-performance shape-memory alloy has been developed by the metallic materials research team of Tohoku University, Sendai, Japan. Compared with conventional shape-memory alloys, $Ti_{50}Ni_{50-x}Cu_x$, x = 0–20 at.% features: 5–6 times greater thermal energy convertibility, 100 times greater corrosion resistance in a rapidly solidified material, and a transformation temperature range as narrow as 6.5°C.

The new alloy contains a fine columnar microstructure with high crystal anistropy and a homogeneous smooth surface to less than 1 μm. It was developed by applying the rapid-quenching process used to produce amorphous metals. The new shape-memory alloy is considered ideal for producing shape-memory composite materials and micromachines, and also for heat engines with narrow temperature ranges for transformation.

Copper is known to improve the strength of shape-memory alloys and to narrow the transformation temperature range. Adding 8–10% copper, however, has been the upper limit using the conventional manufacturing process (i.e. melting and mechanical working); also, at higher copper concentrations the alloy became brittle and manufacturing was more difficult.

Rapid quenching was introduced to control the cooling rate of the melt and to optimize the crystalline grains prior to a transition to the amorphous state. This allows continuous manufacturing of Ti-Ni-Cu memory alloy ribbons, 2–4 mm wide and 30–120 μm thick, containing hyperfine columnar crystals less than 1 μm in diameter and featuring excellent crystal orientation isotropy.

The shape-memory effect and other material functional properties can be improved by rapid solidification. In particular, the thermal-energy convertibility reached the maximum value, 5–6 times greater than that of the conventional types, with a copper content of 13%, the transformation strain of the shape memory was doubled, and the transformation temperature range (for 17% copper) decreased to a minimum of 6.5°C. Also, the thermal fatigue resistance was increased 10-fold, and the corrosion resistance and vibration damping properties were also improved considerably.

The improved characteristics, especially the 10-fold improvement in thermal fatigue resistance, is attributed to the simultaneous phase change in each grain of the material, since it has a monocrystalline structure (columnar grains oriented the same way), so that there is a minimal internal friction loss during the phase transformation compared with conventional types of random polycrystalline structures.

A paper on this research ("Improvements of Shape Memory Effect and Damping in Rapidly Solidified TiNiCu Alloys" by Y. Furuya at the Department of Materials Processing and Engineering, M. Matsumoto of the Research Institute of Minerals and the Institute for Advanced Materials Processing, and H.M. Kimuya and T. Masumoto of the Institute for Materials Research) will be presented at the International Conference of Shape-Memory Materials '94, September 26–30, 1994, Beijing, China.

F.S. Myers

Worcester Polytech Receives $1.4 Million for Clean Metal Casting Research

Worcester Polytechnic Institute in Massachusetts is the recipient of a $1.4 million five-year cooperative agreement from the Department of Energy for research in clean metal casting, particularly aluminum casting alloys. The research will be performed at WPI's Aluminum Casting Research Laboratory (ACRL), an industry-sponsored laboratory dedicated to advancing aluminum casting technology. The principal researcher will be Makhlouf M. Makhlouf, ACRL director and research associate professor of mechanical engineering at WPI.

Scrap castings are estimated to account for more than $130 million per year in wasted energy and materials. "Implementation of the economical, in-process, precasting, metal cleanliness assessment methods that we hope to develop will reduce scrap by at least 20 percent and result in substantial material and energy savings," says Makhlouf. WPI will study two classes of contaminants that prevail in molten aluminum—hydrogen and inclusions.

"Technology transfer of this research to the U.S. metal casting industry and the public is important and WPI will be conducting an annual workshop for the industry to share the results of the research," said WPI Provost Diran Apelian, Howmet Professor of Mechanical Engineering. WPI will also hold advisory meetings with the industrial participants. Plans also include an industrial internship program, a national toll-free hotline, newsletters, educational tutorials, use of multimedia and interactive video, documentation of the knowledge base, and benchmarking.

Others directly involved in the research with Makhlouf and Apelian are research associates Libo Wang and Allaudin Ahmed, and Charles E. Eckert, adjunct professor of mechanical engineering at WPI and president of Apogee Corp.

The ACRL Consortium

The ACRL Consortium is funded primarily by a consortium of companies from the aluminum casting industry; additional resources are provided by the federal government. The laboratory, which is affiliated with WPI's Department of Mechanical Engineering, is totally dedicated to applied research on topics pertaining to cast aluminum alloys. Current member companies are as follows:

Primary Producers—Alcan International Ltd., Aluminum Company of America, Commonwealth Aluminum, Pechiney Corporation, Reynolds Metal Corporation.

Foundries—CMI Technical Center, Consolidated Metco, Doehler-Jarvis, Hitchcock Industries Inc., Intermet Corporation, Littlestown Hardware & Foundry, Stahl Speciality.

End Users—Ford Motor Company and General Motors.

Foundry Suppliers—KB Alloys Inc., Metaullics Systems Co. LP, Selee Corporation, Shieldalloy Metallurgical Corporation.

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New Design Points Toward a Low-Cost, High-Efficiency Solar Cell

An innovative solar cell design employs low-cost, low-quality materials to produce cells that could, if they are successfully mass-produced, cut costs 80%, making them competitive with conventional power sources. This work is being performed at The Center for Photovoltaic Devices and Systems located at the University of New South Wales near Sydney, Australia.

The new cell uses a multilayer structure and buried contact technology. The cell is basically designed like other crystalline cells with sunlight striking two different active layers—the n layer with negative electron charges and the p layer with positive charges. The moving charges are then gathered into electric current.

Existing designs use high-quality crystals to produce electricity because the charges must travel a distance of 200 microns from the interior to the boundary area of the layer. In addition, the charges flow without encountering any flaws or defects that would prevent them from contributing to the current. In the new design, thin alternating n and p layers provide tolerance to low-quality material by shortening the distance charge carriers need to flow without encountering flaws and defects. The thickness of each layer, 3 μm, is chosen to be smaller than the minority carrier diffusion length within that layer. This means that all carriers generated by sunlight within the multilayer stack will be collected and will contribute to the output current of the module.

Although silicon is now used as the substrate, a glass substrate will eventually serve as the base of the cell. A multilayer stack is deposited onto it by a technique such as chemical vapor deposition. The first layer is a dielectric such as silicon oxynitride/nitride followed by several layers of silicon of alternating doping polarity. Finally, a silicon oxynitride/nitride serves as the capping layer. Textured surfaces encourage light trapping within the deposited stack. With a total thickness of 20–30 μm, the cell uses much less silicon than regular commercial cells with thicknesses of 300–400 μm.

After formation of the cell, a laser cuts grooves in the stack so that all the n layers can be connected to each other and all the p layers can also be connected to each other in parallel. Metal contacts are then laid into the grooves. Both sides of the stack are then covered with a transparent material. The back would also absorb solar radiation and produce energy. The basic module size would be 1 m^2 in area, a factor of 100 times larger than the basic production unit with a size of 100 cm^2.

MEC Joins with Penn State to Offer Interactive Video Courses

The Materials Education Council (MEC) is working with Pennsylvania State University to offer two materials-related distance learning courses in a new format called VTLA, Videotape Live Audio. Starting in 1995, videotaped lectures will be sent to participating universities to cover two of three weekly course hours. The third hour will be a call-in question-and-answer period with the presenting professor. Questions and answers will be heard by all students at all sites.

Departments interested in generating a new course offering can participate in a faculty development program. A faculty member can be "apprenticed" to the course and prepare to teach it independently within a year or two.

The first two courses to be offered in 1995 are: "Synthesis of New Materials; Serendipity Plus Science" by Rustum Roy, Penn State, in the spring and "Smart Ceramics" by R.E. Newnham, Penn State, in the fall.

For more information, contact Dr. Robert Berrettini at MEC (814) 865-1643, fax (814) 863-7040. Only a limited number of departments can be accommodated in the live discussions.

Strong, Erosion-Resistant Concrete Can Use Recycled Polystyrene

A concrete that contains recycled polystyrene and is stronger and more resistant to erosive chemicals than ordinary concrete has been developed at Oak Ridge National Laboratory. The concrete could be used to contain toxic wastes safely, build sturdier and lighter weight bridges, and pave highways that would develop fewer potholes and require less repair, say its developers.

Other polymer-impregnated concretes have been developed, but their performance has been limited by the water they contained. Al Mattus and Roger Spence of Oak Ridge's Chemical Technology Division, however, developed a way to pack polystyrene in all the pores of the concrete even when water is present.

Six years ago, Mattus and Spence began studying the use of dense, cement-based (or grout) waste forms to isolate nitrate, a nuclear fuel reprocessing waste that tends to migrate when in contact with water. Their work expanded to include the use of polymers to block internal pores of the grout waste-form to slow nitrate migration.

"We achieved total saturation of the concrete with polymer by using pore-entry particles that open a network of channels inside cement-based grout despite the presence of water," says Mattus. The method requires no special equipment and appears to be easily adaptable to practical industrial scale-up.

According to Oak Ridge sources, representatives of the New York Port Authority are evaluating the possible use of the concrete as a protective coating for New York City piers that are being eroded by seawater. □

CORRECTION: Author Evan G. Colgan's biography on p. 19 of the August 1994 MRS Bulletin should have read as follows: "Colgan received his BS degree in applied physics from the California Institute of Technology and his PhD degree in materials science and engineering from Cornell University in the area of thin film aluminide formation."

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