

# Nanostructured Materials Get Tough

**T**he central tenet of materials science is that the properties of a material are determined by its structure and yet, until quite recently, we have had only the grossest control over the structure of most materials. For example, live steel (steel containing oxygen that forms fizzy carbon monoxide bubbles as it cools) tends to produce an ingot with an exceptionally clean skin, or rim layer, but an inhomogeneous interior. For many years steel sheets for the outer panels of automobile bodies were made from the skin of live-steel ingots to take advantage of its superior cleanliness. Nature determined and the engineer merely selected.

Decades of research have finally put the structure of some materials under our control, allowing us to determine as well as to select their properties. Among the new designer materials are nanostructured, or

nanophase, materials—dense, ultrafine-grained solids with a high percentage of atoms at grain boundaries. Whereas in conventional polycrystalline materials grain boundaries account for less than 1% of the volume, in nanostructured materials they can occupy as much as 50%. The predominance of atomic structures typical of grain boundaries leads to marked improvements in properties such as corrosion resistance, wear resistance, strength, and hardness.

Nanostructured materials have the reputation of being fairly expensive but in fact the cost penalty varies greatly from application to application. The recent sprouting of many small companies marketing nanostructured materials suggests that in selected cases the improvement in properties outweighs the higher processing costs. Among those cases are “hard metal” parts, read

heads for high-density magnetic storage, toner powders for use in high-quality color copiers, nanocrystalline metals used in transformer cores, metal catalysts, ceramic powders that are pressed into “net-shape” parts, multilayer protective coatings, and optical coatings transparent to some wavelengths but opaque to others. By comparison with these exquisitely engineered materials, the rim layer of a live-steel ingot is a ham-fisted affair indeed.

## Manufacturing processes

The key enabling factor for industrial exploitation of these materials is the development of cost-effective, large-scale manufacturing processes. Nanocrystalline materials were first synthesized in the early 1980s in Germany using gas condensation. Today there are more than 30 different processes

for their manufacture, including ones based on chemical vapor deposition, physical vapor deposition, reactive sputtering, laser pyrolysis, spray conversion, mechanical alloying, and sol gel. However, many of these are expensive, require sophisticated equipment, and have low production rates.

“The main barrier [to commercialization], especially at genuine nanoscale, is that most of the work is done in laboratories at small scale,” said Arun Ranade, president of Particle Technology (Hanover, MD). “In order for the materials to be used in industry, the costs have to come down. The process itself

is not very expensive, but to make enough material to sell is a challenge, because the demand is rapidly catching up to production thresholds.”

Nanophase Technologies (Burr Ridge, IL) has developed a process based on gas-phase condensation that is significantly faster and cheaper. In gas-phase condensation, a precursor material is heated until it vaporizes, and the vapor is then condensed on a surface cooled with liquid nitrogen. The process is cumbersome because it is typically done in a vacuum. In the new process, called physical vapor synthesis (PVS), the precursor is heated by a plasma in an open atmosphere and the vapor is cooled by collisions with the atoms of a reactive gas. PVS allows Nanophase to produce tons of materials per year at a cost as low as 10 cents per gram, whereas in 1989 the price tag was \$1,000 per gram.

When it comes to multilayered materials, the microstructure is typically determined during synthesis by controlling the thickness of the layers. According to Troy Barbee, a senior scientist at Lawrence Livermore National Laboratory, the drawback of this technique has been that only comparatively thin structures could be produced in this way—typically ones thinner than 1  $\mu\text{m}$ . Barbee has developed sputter deposition processes that allow construction of multilayer materials as thick as 0.5 mm that consist of as many as 50,000 layers.

Nanometals (Kingston, Ontario), formed under the auspices of Parteq Research and Development Innovations, a not-for-profit corporation that acts as a technology-transfer agent for Queens University in Ontario, has adapted a commercial electrodeposition method using plating baths to the manufacture of nanostructured metals. The process is more practical than other methods of making nanostructured materials, according to John Molloy, executive director of Parteq, because it is fast and can be used to produce bulk material, foils, and coatings of any shape. Many companies already own the needed equipment, and the scaled-up process could be combined easily with standard commercial electroplating processes, including electroforming and reel-to-reel plating.

Particle Technology has developed a turbulent vapor-phase reactor technology that provides good control over particle size and purity for production of kilogram quantities of oxide and nonoxide particles for advanced ceramics and pigments. It is now working to further commercialize this technology and extend it to the preparation of nanosized powders for application as catalysts and electronic materials.

Nanodyne, Inc. (New Brunswick, NJ) uses a spray conversion process to produce tungsten-carbide-cobalt composite powder with a grain size smaller than 15 nm. The powder is used to make "hard metal," a sintered alloy as hard as diamond that is used to make cutting tools, drill bits, armor plate, and jet-engine parts. According to Purnesh Seegopaul, senior vice president of operations, the process creates large particles containing millions of grains, which act like a kind of in situ packaging that makes the material easier to handle.

## Electronics applications

Electronics is expected to yield some of the best opportunities for nanostructured materials because ongoing miniaturization in that industry has produced correspondingly strong demand for new materials.

A new class of materials that exhibit the giant magnetoresistance effect (GMR) could make it possible to achieve ultrahigh-density data storage by improving the sensitivity of read heads. These materials consist of alternating layers of a magnetic material and a conductor. Depending on the thickness of the conductor, the spins of atoms in successive layers of the magnetic material assume parallel or antiparallel alignments. When a magnetic field is applied to the material, the magnetization of one layer reverses direction and the material's electrical resistance either decreases or increases, depending on the original alignment. The change in resistance is typically 10 to 50 times larger than the change in conventional magnetoresistive materials. The field strength needed to reverse the magnetization direction, which was originally fairly high, is now less than 100 Oe. R.D. Shull, who heads work on GMR materials at the

National Institute of Standards and Technology (NIST), estimates that within a decade, GMR-based data storage products will account for billions of dollars in annual sales for U.S. companies.

In 1995 NIST opened a new Magnetic Engineering Research Facility designed to resemble a commercial magnetic thin-film manufacturing facility, but one with access to the most advanced structural and magnetic diagnostic techniques. Industrial collaborators include IBM, Seagate, Hewlett-Packard, Nonvolatile Electronics, Read-Rite, and Motorola, which is developing a GMR-based version of dynamic random access memory (DRAM). "Our role is to investigate the science underlying the manufacturing process, something these companies cannot afford to do on their own," said Shull.

NIST researchers are also seeking to optimize the processing of magnetic nanocomposites for use as toner materials in high-quality color copiers and printers. Xerox recently set up a pilot plant to produce large quantities of gamma  $\text{Fe}_2\text{O}_3$ /polymer nanocomposites for use in copiers. In addition, Shull hopes to convince the refrigeration industry to use nanocomposites as refrigerants in magnetic refrigerators, an environmentally friendly alternative to coolants such as Freon used in traditional gas-compression refrigerators.

According to Molloy, nanocrystalline metals are well suited for electrical applications that demand both good magnetic properties and superior hardness, wear, and corrosion resistance. They are excellent soft magnets and yet, because electrons are scattered at the grain boundaries, they have relatively high electrical resistivity, which reduces eddy current losses in electrical applications. Nanometals sees small transformers, power supplies, and high-efficiency motors as promising applications, and has already licensed its technology to Ontario Hydro Technologies for use in transformer cores.

## Chemicals and ceramics

Nearly spherical nanocrystalline powders are popular for applications in chemical catalysis, especially in the pharmaceuticals

industry. According to Donald Freed of Nanophase, because the proportion of atoms at the surface increases as particle size decreases and because surface atoms are more reactive than bulk atoms, nanometer-sized spherical particles of a noble metal catalyst can be several times more active than

ordinary-sized particles. For this reason, Nanometals is developing nanocrystalline alloys of nickel-molybdenum as advanced electrode materials for high-efficiency alkaline fuel cells.

In addition, nanostructured materials are beginning to find application in the manu-

facture of ceramics. Ceramic parts have traditionally been made by firing a blank that is then machined to the desired shape. Nanophase, however, has developed a “net-shape” process in which parts are made by filling a mold or die with a colloidal suspension of a ceramic powder and applying modest heat and pressure. The powder conforms to the shape of the mold or die, and only minimal polishing is required to finish it.

Net-shape processes offer substantial economic advantages—the final deformation process takes a mere 15 minutes compared to the 6-8 hours needed to machine blanks—but the parts it produces are also very fine-grained and durable, since the flaws typically introduced during machining are eliminated. Using this process, Nanophase manufactures wear-resistant parts for a large equipment manufacturer that aren’t significantly more expensive but last ten times longer than machined ceramic parts.

## Coatings

Near-term applications for nanoscale multilayers include protective coatings, such as thermal barriers, and ultrahard or wear-resistant coatings. According to Shull, structures made by physical vapor deposition will already account for as much as 2% of the estimated \$25 billion high-performance coatings industry in the U.S. within the next decade as dependence on environmentally hazardous electroplated hard chrome decreases. Such high-performance coatings are used in automotive engines, aircraft engines, cutting and machine tools, and equipment for manufacturing ceramic parts.

Nanophase has developed nanostructured transparent coatings for cathode ray tubes used in televisions. The coatings are transparent to visible light but impede electromagnetic radiation at other frequencies. “One of the unique properties of our nanocrystalline materials is that when they’re dispersed properly, the particles are a tenth or less of the wavelength of typical visible light,” said Freed. “So you can make a transparent coating that has electrical functionality, such as conductance.” The Structured Materials Institute (SMI) in Piscataway, NJ, plans to manufacture

nanograined windows for high-temperature applications that are transparent to visible light but opaque to the infrared.

## Future challenges

Most of the remaining challenges in the commercialization of nanostructured materials are financial rather than technological. “There’s no one big hurdle that needs to be overcome anymore; rather, there are many hurdles in each individual development effort, since each material has its own chemistry and its own set of problems to be solved,” said Gary Tompa, president of the SMI. Remaining challenges include broadening the range of materials, driving down costs, and improving quality and purity, especially of materials that are used in areas with exacting demands, such as electronics and catalysis.

In fact, Molloy predicts that the market for nanostructured materials will experience a sharp upsurge within the next three to five years. “I think we’re sitting on a very big opportunity, and when people realize what can be done with these materials, and that we can make them very economically, they will be very interested in using them.” 