by Diana Lutz

Putting Quasicrystals to Work

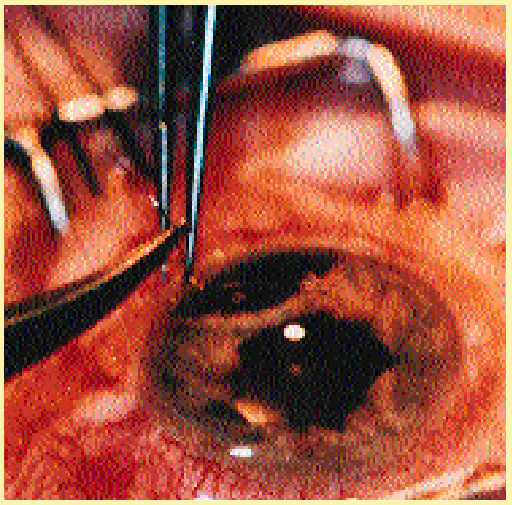
At a conference held August 19-23 in Ames, Iowa, “New Horizons in Quasicrystals: Research and Applications,” Jan-Olof Nilsson, manager of physical metallurgy for the R&D Centre of Sandvic Steel, Sandviken, Sweden, said: “Three years ago I thought that quasicrystals were something that existed only in the academic world, but I have been forced to change my mind. As a matter of fact, we can’t avoid quasicrystalline precipitates in our commercial materials, and furthermore, we can make use of them.”

In the past several years many people have changed their minds about quasicrystals, the new form of matter discovered in 1982. (Quasicrystals differ from glasses in that their atoms are arranged in orderly patterns, and from crystals in that these patterns do not repeat periodically; see Figure 3, page 29.) At first quasicrystals were considered of academic interest only, but they may end up in many applications.

Quasicrystal characteristics

The first quasicrystals were metastable, a property that more or less precluded applications because it meant the structure might vanish if the material were reheated. But within a few years stable quasicrystals were found in several different materials systems, including aluminum–copper–iron (Figure 1) and aluminum–palladium–manganese. Once the initial uproar over structure died down and large samples of stable materials were available, many different laboratories began to examine their properties.

These turned out to be quite different from the properties of crystalline metals. Quasicrystals, for example, are extremely poor electrical and thermal conductors. The thermal conductivity of quasicrystals containing more than 70 atomic percent aluminum is two orders of magnitude below that of aluminum and roughly equivalent to that of zirconia, which is used as a refractory material. Quasicrystals are also exceptionally hard, and their surfaces have very low coefficients of friction, good wear resistance, and good oxidation and corrosion resistance. Depending on how they are prepared, quasicrystals can have coefficients of friction so low they are comparable to the coefficient of a diamond gliding over a diamond film.



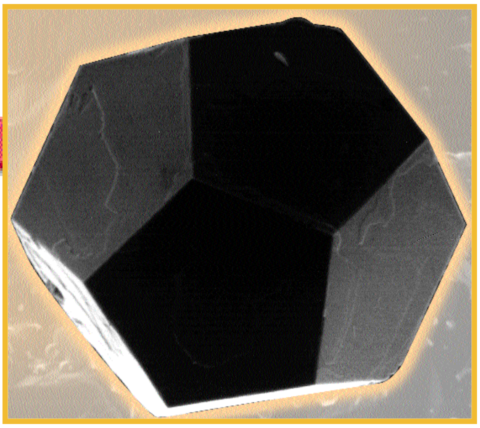
Sandvic Steel

Figure 2. The first bona fide application of quasicrystals is a steel alloy produced by Sandvic Steel that is made into medical instruments. These must be easy to form, yet very strong, to avoid breakage during use.

At first, there was an apparent obstacle to exploiting these properties: Bulk quasicrystalline materials are brittle at temperatures below a few hundred degrees Celsius. This problem was soon solved; quasicrystals made into coatings by the standard techniques of metallurgy, such as atomization and plasma spraying, retain the desirable properties, but not the brittleness, of the bulk material. Most applications now under discussion use quasicrystals as coatings, thin films, or small particles embedded in another material.

Exploring applications

This summer’s conference was the first to look seriously at quasicrystal applications. [Conference proceedings will be published by World Scientific Publishing, which can be reached by telephone (800–227–7562) or on the Web (http://www.wspc.com).] It was chaired by Alan Goldman, Daniel Sordelet, and Patricia Thiel of the Department of Energy’s Ames Laboratory, in Ames, Iowa, and by Jean-Marie Dubois of the École des Mines in Nancy, France.



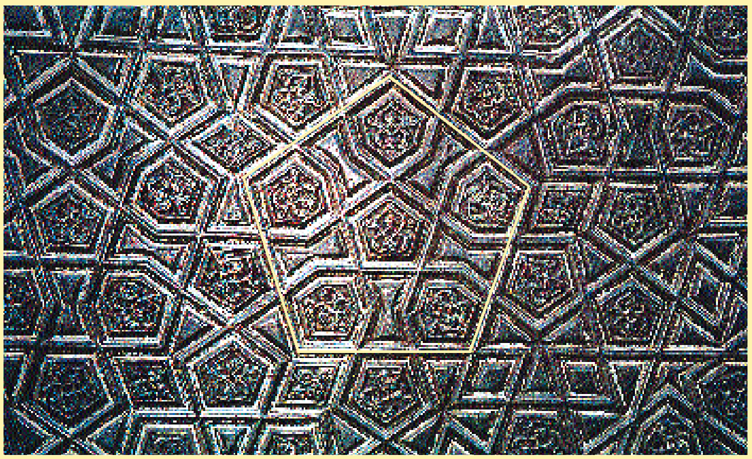
Ames Laboratory

Figure 1. This aluminum–copper–iron quasicrystal, shown in a secondary electron microscope image, belongs to the icosahedral family of quasicrystals, and has 12 pentagonal faces.

Pinpointing the first instance of the commercial use of quasicrystals is a bit tricky, because there were some early “stealth” applications. Dan Shechtman of Technion-Israel Institute of Technology (Haifa, Israel), who discovered quasicrystals, remarked in passing that 1890—an aluminum–lithium alloy, developed by Alcan Aluminium Limitée in Montreal, that is now one of three standard aluminum–lithium alloys used in the aerospace industry—sometimes contains quasicrystalline precipitates. Still one can reasonably argue that Sandvik Steel’s alloy, which is made into surgical and acupuncture needles and dental reamers, is the first bonafide commercial application.

Nilsson began his talk about this alloy by asking the audience to imagine the consequences of a needle fracturing during ophthalmic surgery (Figure 2); as this exercise suggests, wire that is made into surgical needles must have high strength, preferably in excess of 2,500 megaPascals (mPa), but it must be easy to form into delicate shapes. Both requirements can be met if the material responds well to tempering, or aging, because it can be formed in a fairly soft state and strengthened by the application of heat.

“One of the first observations we made



Mehmet Erbudak

Figure 3. Quasicrystals, with their five-fold symmetry, are ordered but do not repeat at regular intervals, just like Penrose tilings, or these decorations on the west-entrance door, Sultan Ahmet Mosque (17th century), Istanbul, Turkey.

about this alloy," Nilsson said, "is that the tempering effect is quite strong, much more than was required." In some cases, tempering increased the alloy's strength by as much as 800 mPa. Moreover, as long as the alloy was held at temperatures below 500 °C, it hardened continuously, all the way up to 1,000 hours of aging. "This is quite exceptional," Nilsson commented. "Spring materials are usually tempered for four hours, after which softening occurs. I've never seen a material that hardens all the way up to 1,000 hours of aging."

Intrigued, he set himself the task of figuring out the relation between the material's microstructure and its properties. "Of course, in a steel company, we are happy just to get a patent for an alloy with unusual properties," he said, "but I am of an inquisitive nature, so I wanted to understand why this alloy had these properties."

The unaged material was virtually all heavily dislocated martensite (carbon steel) and contained almost no precipitates. When it was aged at 475 °C for 100 hours, however, dense precipitates formed within the martensite. X-ray diffraction studies demonstrated that most of these precipitates were icosahedral quasicrystals.

Nilsson concluded that these quasicrystalline particles produced the alloy's high strength and remarkable immunity to overaging. The hard quasicrystalline particles strengthen the steel much as the glass fibers strengthen fiberglass. After prolonged tempering, the precipitates in a precipitation-hardened metal usually have grown larger than their optimum size, a process called coarsening. The quasicrystalline precipitates, however, are very slow to coarsen, probably because they have very low surface energy.

Soft strength

Akihisa Inoue of the Institute for Materials Research at Tohoku University in Sendai, Japan, deliberately set out to exploit the strengthening properties of quasicrystalline particles. Bulk aluminum–manganese quasicrystals are both hard and brittle at temperatures below 1,000 °C because dislocations can move only with difficulty through the quasiperiodic lattice. The goal of Inoue's team was to create alloys of similar composition that would retain some of the desirable characteristics of the binary quasicrystal but be easier to deform.

By melt-spinning (rapidly cooling) aluminum–manganese–lanthanide and aluminum–chromium–lanthanide alloys, Inoue's team forced a unique solidification process that produced alloys consisting of nanoscale quasicrystalline particles surrounded by crystalline aluminum. The hard quasicrystalline particles endow these alloys with the strength pure aluminum lacks, and the soft aluminum endows the alloys with the ductility quasicrystals lack. The alloys have good bending ductilities, and they also exhibit yield stresses of 1,200–1,400 mPa.

The team produced a similar microstructure in larger samples by extruding mixed-phase aluminum–manganese–cobalt powders that had been produced by high-pressure gas atomization. These alloys had somewhat lower yield stresses (500–850 mPa), but they also exhibited elongations greater than those of alloys of comparable strength.

Titanium techniques

Some applications exploit properties of quasicrystals other than their mechanical ones. Ken Kelton of Washington University in St. Louis, Missouri, spoke about the possible use of titanium-based quasicrystals, particularly titanium–zirconium–nickel, for hydrogen storage. "Hydrogen likes to sit in tetrahedral sites in transition metals," Kelton said. "We believe that quasicrystals and their approximants have a huge number of these tetrahedral sites. In addition, hydrogen likes certain kinds of chemistry. It doesn't work well with aluminum, but it works beautifully with titanium, zirconium, and the rare earths. So the titanium quasicrystals have the combination of a favorable chemistry and a favorable structural unit."

Kelton and his colleagues found that titanium–zirconium–nickel quasicrystals can absorb nearly two hydrogen atoms per metal atom—more hydrogen than is absorbed by related crystalline and amorphous materials. Moreover, it is more hydrogen than is absorbed by the hydrogen-storage materials currently in use, such as the lanthanum–nickel compounds in renewable batteries in laptop computers. "We can store almost double the weight percent of hydrogen that can be stored in lanthanum–nickel-5," Kelton said.

This application still faces some obstacles. Titanium–zirconium–nickel tends to form a surface oxide that can delay hydrogen loading. "This is not uncommon," Kelton commented, "and we can get around it by gently milling the quasicrystal ribbons or by electrolytic loading." He also noted that titanium-zirconium–nickel has so far been produced only by melt-spinning. Although the quasicrystal is stable, the reactivity of titanium has prevented it from being produced by the more versatile techniques used to make aluminum-based quasicrystals.

Solar absorption

Thomas Eisenhammer, of TiNO$_x$ Gesellschaft für Energieforschung und Entwicklung in Munich, Germany, described the potential of quasicrystals for a solar-selective absorber, which absorbs solar radiation and converts it to heat. Eisenhammer stressed that quasicrystals “do not provide extremely exotic optical properties” that would make them runaway favorites in the marketplace. He nonetheless foresees that, in some environments, their corrosion and abrasion resistance would give them an edge over other candidates.

The ideal solar-absorber material shows large absorption in the solar spectrum and is highly reflective at longer wavelengths. These characteristics allow it to function much like the windows of a closed car; sunlight comes in and is absorbed by the seats, but any energy re-emitted as infrared radiation is trapped in the car by the windows. The car’s interior, accordingly, becomes much hotter than its exterior. By similar means, solar-selective absorbers can reach temperatures as high as 500°C.

The optical properties of quasicrystals are markedly different from those of typical conductors and dielectrics. The reflectance of bulk quasicrystals such as aluminum–palladium–manganese is about 60% over a wide wavelength region. Good conductors, such as silver, have reflectances close to 100%, and even metals with lower conductivities have reflectances higher than those of quasicrystals. Dielectrics, on the other hand, have much lower reflectances than either quasicrystals or metals, but they have high transmittances.

The closed-car effect can be achieved by appropriately combining the optical properties of these materials. Eisenhammer reported that a thin-film stack—composed of a layer of quasicrystalline aluminum–copper–iron between two layers of the dielectric alumina—deposited on a reflective metal had a solar absorptance of 90% and a room-temperature emittance of about 2.5%. He suggested, however, that it might be possible to achieve even better properties, particularly lower emittance, by substituting a film consisting of quasicrystalline particles in an alumina matrix for the homogeneous quasicrystalline film.

A number of other applications were mentioned at the conference in Iowa. Shechtman estimates that some 20 patents have been issued for quasicrystal applications. Among these are patents for precipitation-hardening of steel, radiation conversion, photomagnetic recording, nonstick surface coatings, and heat barriers. [Further updates will be available at the 6th International Conference on Quasicrystals in Tokyo (May 26–30, 1997). You can find more information on the Web (http://coral.t.u-tokyo.ac.jp/icq6).]

Despite the difficulty of bringing a new material to market, many conference participants were cautiously optimistic. The first products are already out the door, and other contenders are lined up at the gate. Exciting times could be ahead for quasicrystals.