

Research in Progress

Amorphous Alloys

AMORPHOUS metals are alloys whose atoms do not line up neatly in the regular periodic array of a crystal but rather in the more disordered arrangement of a liquid or glass ("New Materials: Atomic-Scale Architecture of Metallic Solids," *E&S* May-June 1980). This structure makes amorphous, or glassy, metals stronger and more wear- and corrosion-resistant than their crystalline counterparts and also confers on them superior electrical properties useful, for example, in cross-country power transformers.

The only trouble with these promising new materials is that it's not so easy to alter atomic structure and make it stay that way at normal temperatures. Manufacturing methods still depend on a basic process developed in the 1960s by Caltech's Pol Duwez, now professor of applied physics and materials science, emeritus. This involves cooling a liquid metal so rapidly (at a rate of a million degrees per second) that it doesn't have time to crystallize and retains instead its liquid atomic structure. Current fabrication techniques can turn out amorphous metals only as ribbons, necessarily thin in order to remove the heat quickly. No one has, until now, figured out a way to directly make metallic glasses in bulk.

William Johnson, associate professor of materials science, thinks he has found a way. With Ricardo Schwarz, a visiting associate last year and now at Argonne National Laboratories, he has developed a method of growing thin layers of amorphous metals at relatively low temperatures. Thin layers aren't much of an improvement over ribbons; but

since there is no necessity of a rapid cooling process, Johnson sees no fundamental reason why the process won't work in bulk as well as in layers.

An accidental discovery by graduate student X. L. Yeh and research fellow Konrad Samwer that hydrogen would diffuse into a crystal of zirconium and rhodium, making it amorphous, led to the new process. By itself the discovery wasn't particularly interesting. But to Johnson and Schwarz it signaled the possibility that the same thing might happen with known pairs of metals that exhibit "anomalous fast diffusion"; that is, one metal can move rapidly through the other at low temperatures. At low temperatures where the atoms have little freedom to move around, the easiest structure for the resulting alloy to form is a glass.

The two scientists experimented with a number of these pairs including gold-lanthanum, gold-yttrium, nickel-hafnium, and nickel-zirconium. Johnson believes there are many other good candidates for the process, including nickel-titanium and iron-titanium, alloys that are used for high-temperature applications, and carbon-iron, better known as steel.

By evaporating submicron-size metal layers, Johnson and Schwarz built up alternating layers of thin films of, for example, gold and lanthanum. When heated to 100°C, high enough to produce a reaction but low enough to prevent growth of crystalline compounds, anomalous fast diffusion occurred at the layer interfaces, and an amorphous alloy was formed. The process has to be ther-

modynamically allowable, so the two metals must react exothermically; that is, the reaction must produce energy and move toward equilibrium, so that the glass is more stable than the original crystalline state. Actually what occurs in the process, says Johnson, is a matter of "tricking nature into a constrained equilibrium."

Although they don't yet have any experimental evidence, Johnson expects the process to work in three as well as in two dimensions — just mix the metal powders together, compact the mixture so there are no holes, heat it up a bit, and it should become a chunk of metallic glass. But first he wants to understand the science of what's going on by "getting the theory of the reaction sorted out." He's collaborating in this work, which has been supported by the Department of Energy, with a group at JPL under Satish Khanna. They want to know, for example, how far the amorphous alloy layer will grow through a layer structure before it crystallizes. Such experiments will tell the scientists what size grains of metal powders can be used; it may be possible to use grains of micron size or tens of microns, more standard sizes that would be of considerable advantage in commercial applications. They also need to determine and control the times and temperatures necessary for the process and figure out how to eliminate such problems as surface oxides on the metal powders. Solutions to these problems may well lead to a process capable of producing large structures of amorphous metals cheaply and easily. □ — JD

Fading Fast

ART IS LONG, though life is short, time fleeting, and so on, according to centuries of poets. But some works of art may not last long enough. Research at the Environmental Quality Laboratory has established that ozone, a prime ingredient of modern air pollution, is a threat to certain artists' pigments.

Ozone, formed by photochemical reactions between hydrocarbons and oxides of nitrogen, attacks organic materials, particularly at unsaturated double bonds. Besides being the culprit in the respiratory irritation familiar to inhabitants of smoggy areas, ozone has been implicated in cracking rubber, fading textile dyes, and erosion of the binder in painted exterior surfaces. But while art works are known to fade in the presence of light and oxygen, ozone, a more powerful oxidant than oxygen, can apparently cause the deterioration of some pigments even in the dark.

Glen Cass, assistant professor of environmental engineering, and Cynthia Shaver Atherton, BS '83 (working together with James Druzik of the Los Angeles County Museum of Art), prepared two sets of common artists' watercolor samples applied on watercolor paper. One set was kept in a dark place as a control and the other placed in a light- and air-tight chamber, where it was kept for 95 days with no light, at constant temperature and humidity, and exposed to 0.40 ppm ozone. They also included two Japanese woodblock prints (by Hiroshige) in the experiment, neither one an original, but printed by traditional techniques.

Before and after being exposed to the



When exposed to ozone, the yellow of the hut roofs and the mat at left, as well as the blue-green of the foreground, faded noticeably in this Japanese woodblock print, an early 20th-century half plate reproduction of Minakuchi from the Hoeido Tokaido series by Hiroshige.

ozone, all the samples were characterized according to a standard system by hue (gradation of color in reference to a color wheel), value (lightness or darkness in relation to a neutral gray scale), and chroma (departure from a neutral gray of the same value). Reflectance of the samples was measured at red, blue, and green wavelengths by a microdensitometer, and at continuous wavelengths by a spectrophotometer, and high-quality photographs were taken of all the samples. The latter was especially important for the woodblock prints, since there were no controls.

During the three-month exposure, several of the pigments faded dramatically. One of them, alizarin crimson, is a widely used red pigment consisting of an organic anthraquinone colorant in an aluminum complex (a combination known as a lake). Two other close relatives of alizarin crimson also faded significantly — crimson lake and purple lake, which consist of anthraquinone bound to different metal compounds. The scientists suspect that the chemical process at fault is ozone's cleavage of the anthraquinone molecular ring structure.

The researchers also observed a change in hue, from purple to more bluish, in the mauve pigment, which is a blend of copper phthalocyanine and triphenylmethane lake. Apparently the latter faded (it has also been shown to oxidize rapidly in light), leaving the blue

phthalocyanine behind. The yellow pigments in the Japanese prints also faded noticeably. Although the scientists could not determine precisely the composition of these pigments, chemical tests suggested that they were either gamboge or turmeric, both of which contain exposed carbon-carbon double bonds and aromatic rings that could be attacked by ozone.

The ozone concentration of 0.40 ppm used in the experiments is typical of Los Angeles under heavy smog conditions (although the annual mean concentration is lower by a factor of 10). The research team also measured ozone concentration inside several local art museums. In the Huntington Gallery and the Los Angeles County Museum of Art, which are equipped with activated carbon filters on the air conditioning system, ozone concentrations stayed very low — below 0.01 ppm. In Caltech's Baxter Art Gallery, however, which doesn't have a chemically protected air conditioning system, they determined that the ozone concentration was quite high — about half of that outdoors, which is consistent with others' findings. The three researchers estimate it would take three years outdoors or six years in an unprotected building to equal the ozone exposure undergone in their experiments. Six years for a work of art is hardly long. □
— JD