sive state land use policy, the Land and Water Management Act, based on the ALI model code and concerned with the big cases, stands as a fair mark of Florida's present midway position on the long path toward such a policy. And, given the close conceptual linkage between this Florida law and the pending federal land use policy legislation, the limitations of that law are of national significance.

—LUTHER J. CARTER

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*Erratum*: In the article by Luther J. Carter "Land use Law (I) . . ." (16 November), the last sentence in the second column on page 694 should read, "With some exceptions, little or nothing has been done by either federal or state government to cope with the ultimately more serious problem of protecting the land itself."—

## RECENT DEATHS

**Gordon Alexander**, 71; retired head, biology department, University of Colorado, Boulder; 21 July.

**Orville L. Bandy**, 56; former chairman, geological sciences department, University of Southern California; 2 August.

**Rolf L. Bolin**, 72; professor emeritus of marine biology and oceanography, Stanford University; 22 August.

**Lan Jen Chu**, 59; professor of electrical engineering, Massachusetts Institute of Technology; 25 July.

**Steve Pratt**, 55; professor of psychology, Wichita State University; 28 July.

**Wiley B. Sanders**, 75; former professor of sociology, University of North Carolina; 10 August.

**Howard V. Smith**, 73; professor emeritus of agricultural chemistry and soils, University of Arizona; 10 August.

**C. Martin Spooner**, 71; retired chief, urology department, Toronto Western Hospital; 4 June.

**Harold I. Tarpley**, 75; professor emeritus of electrical engineering, Pennsylvania State University; 8 August.

**T. Ivan Taylor**, 63; professor of chemistry, Columbia University; 27 July.

**James M. Williams**, 97; professor emeritus of sociology, Hobart and William Smith Colleges; 7 August.

**RESEARCH NEWS**

# Glassy Metals: No Longer a Laboratory Curiosity

Ever since a primitive blacksmith first discovered that quenching an alloy of iron and carbon with water could greatly increase the strength of the resulting steel, the world of the metallurgist has been heavily weighted toward the proposition that the most useful properties of metallic alloys often result when nonequilibrium structures are obtained. The principal means for obtaining such nonequilibrium structures has been some variation of the quenching process, that is, the cooling of an alloy so rapidly that the equilibrium structure characteristic of the lower temperature does not have time to form and the high-temperature structure is retained.

Now, the fascination of the materials scientist and solid state physicist with amorphous or noncrystalline materials in combination with the older metallurgical idea of quenching is giving rise to a class of solids known as amorphous metallic alloys or glassy metals. There is a growing interest among theoretical and applied researchers alike in the mechanical, magnetic, and electrical properties of these materials.

When a molten metal or metallic alloy is cooled, the solid phase formed is crystalline, with a structure that depends on the particular alloy composition. In contrast, molten glass-forming materials, when cooled, do not assume a crystalline structure, but instead retain a structure somewhat like that of the liquid—an amorphous structure. In each case, the thermodynamically stable or equilibrium structure at room temperature is crystalline. The difference between the two is in the kinetics or rate of formation of the crystalline phase, which is controlled by factors such as the nature of the chemical bonding and the ease with which atoms move relative to each other. Thus, in metals, the kinetics favors rapid formation of a crystalline phase, whereas in normal glasses the rate of formation is so slow that almost any cooling rate is sufficient to result in an amorphous structure. Glassy metals are formed when the molten metal is cooled sufficiently rapidly that crystallization is suppressed.

There are at least four methods of obtaining glassy metals, only one of which involves rapidly cooling, or quenching, a molten liquid, although all in effect quench by suppressing the rate of crystal formation. The other methods are vacuum evaporation, sputtering, and electrodeposition and "electroless" deposition. The first report of an amorphous metal produced by quenching was that by Pol Duwez' group at the California Institute of Technology, Pasadena; they obtained an amorphous alloy consisting of 75 percent gold and 25 percent silicon by propelling small molten globules against a thermally conductive metal substrate at high velocities. Amorphous specimens produced in this way were foils varying from less than 1 to a few micrometers thick. Alloys made by liquid quenching are limited to one of two groups. The first is composed of alloys made from either a transition or a noble metal and a smaller metalloid element, such as alloys of palladium and silicon or iron, phosphorus, and carbon. The second is composed of alloys made from transition metals only (intertransition metal alloys), such as copper-zirconium.

Vacuum evaporation, in which the starting alloy materials are vaporized by heating in some way and then deposited onto a substrate cooled to the temperature of liquid nitrogen (77°K) or below, is a method for producing thin films of amorphous metallic elements, as well as a wider variety of alloys than by liquid quenching. Sputtering, like vacuum evaporation, can be used to make a wide variety of alloy compositions. A target of the desired composition and a substrate are placed in an ionized gas (plasma) maintained by an electric field. The gas ions are accelerated toward and knock atoms from the surface of the target, which are deposited on the substrate to make a thin film with an amorphous structure. Electrodeposition (the familiar nickel-plating process) is used to make alloys of phosphorus and either nickel, iron, cobalt or palladium.

Most researchers view the amorphous metallic alloys as existing in a thermodynamically metastable phase that can be represented on a modified metallurgical temperature-composition diagram and that is characterized by a well-defined glass transition. The glass transition is in some respects analogous to the phase transition between the liquid and the crystalline solid. In practice, the glass transition is usually observed by measuring the heat capacity as a function of increasing temperature. Near the glass transition, the heat capacity rises rapidly, and it is this rise that is used to mark the temperature of the glass transition. Such measurements were first made in gold-silicon alloys by H. S. Chen (now at Bell Telephone Laboratories, Murray Hill, New Jersey) and David Turnbull of Harvard University, Cambridge, Massachusetts.

The structure of amorphous alloys is thought to be similar to that of liquid metals. One of the first attempts to model the structure of a liquid was that by the late J. D. Bernal of the University of London, who packed hard ball bearings into a rubber vessel in such a way as to obtain the maximum possible density. The resulting dense random-packed (DRP) structure has been the basis for most current attempts to model the structure of amorphous metals.

Calculations of interatomic spacings and the density of the alloy based on Bernal-type models have usually agreed well with the experimentally determined values from measurements on alloys consisting of a noble metal or a transition metal with a metalloid, according to G. S. Cargill III, of Yale University, New Haven, Connecticut, although small discrepancies remain. One difference between real alloys and hard spheres is that the components of an alloy have different sizes, so that models based on two sphere sizes might be more appropriate for a binary alloy. D. E. Polk, now at Allied Chemical Corporation, Morristown, New Jersey, suggested that the smaller metalloid atoms might fit into holes or interstices in the DRP structure of the larger metal atoms. An approximation of a two-sphere DRP model can be constructed with the use of the local atomic configurations of the one-sphere DRP structure by extending them to two sizes of spheres. Cargill now thinks that calculations based on this approximate model indicate much better agreement with experiment than older models. A complete two-sphere structure has yet to be built and analyzed, however.

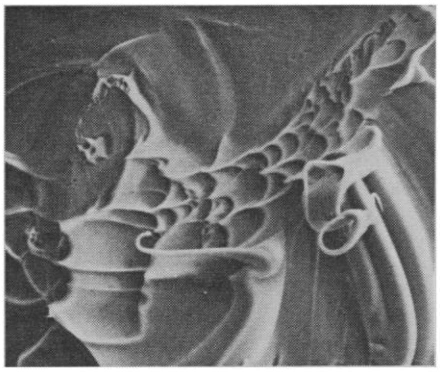

Fig. 1. Scanning electron micrograph of the fracture surface of a glassy metallic alloy deformed by torsion inside the microscope. [Source: H. J. Leamy, Bell Telephone Laboratories]

The main competitor to the DRP model of an amorphous metal is the microcrystallite model, in which the solid is envisaged as being composed of very small crystalline volumes (with dimensions as small as 10 to 30 angstroms) separated by highly disordered regions—that is, a structure like that of a normal metal, but with a nearly vanishingly small grain size. For the most part, investigators of the properties of amorphous metals have decided in favor of the DRP-like amorphous structure, reserving the microcrystallite model for those alloys not cooled sufficiently rapidly to completely suppress crystallization.

Most recently, for example, P. Chaudhari, at IBM's Thomas J. Watson Research Center, Yorktown Heights, New York, has found that the results of x-ray and electron diffraction measurements and of high-resolution transmission electron microscopy on both amorphous semiconductors and metals were consistent only with amorphous random-packed structures. John Vander Sande and Nicholas Grant, at the Massachusetts Institute of Technology, Cambridge, have also used a high-resolution electron microscopy technique, in which the presence of crystal lattice planes could be seen in crystallites as small as 25 Å across, but they observed no lattice planes in amorphous copper-zirconium alloys. Finally, Stewart Solin of the University of Chicago, Chicago, Illinois, on the basis of Raman scattering measurements on microcrystallite and amorphous forms of silicon, diamond, and graphite, found that amorphous semiconductors are not microcrystalline, and by inference, neither are amorphous metals.

A primary reason for the considerable interest in the structure of glassy metals is the wide range of new phenomena that these materials exhibit. For example, one of the most promising properties of amorphous metals is their high strength. Most recently, the Allied Chemical Corporation has announced the development of a new group of glassy metals with high strength and ductility, which can be manufactured inexpensively, in technologically useful quantities and at high rates. The combination of high strength and ductility is extremely desirable. In usual crystalline materials, in contrast, one finds an inverse relation between the two properties—a high strength goes with a low ductility and vice versa. According to Carl Cline at Allied, one can foresee applications involving high-strength wires and ribbons in a variety of areas, although the relatively low temperature at which many amorphous metals crystallize when they are heated may impose some limitations. The ability to overcome what has long been a problem in the area of amorphous metallic alloys, the production of specimens in sizes and shapes suitable for use in practical applications, combined with the relative inexpensiveness of the materials used in Allied's alloys indicates that amorphous materials have entered the stage of being commercially exploitable.

Amorphous metals often exhibit strengths near the theoretical limit of crystals of the same material and are many times stronger than most crystalline materials. Polk and C. A. Pampillo at Allied Chemical Corporation, for example, reported nickel-iron and iron amorphous alloys with fracture strengths (applied stress before the alloys fractured) of the order of 375 × $10^3$ and 350 × $10^3$ pounds per square inch, respectively. Although these alloys are among those developed by Allied specifically for their high strengths, two of the most commonly studied amorphous metal alloys (because they are so easily formed compared to other alloys), palladium-silicon and nickel-phosphorus, have tensile strengths of 200 × $10^3$ and 125 × $10^3$ pounds per square inch, respectively, indicating the pervasiveness of the high-strength characteristic throughout the range of amorphous metallic alloys.

Harry Leamy and his co-workers at the Bell Telephone Laboratories have studied the deformation and fracture of glassy metals. Leamy reported that, in tensile tests of amorphous palladium-silicon, approximately 10 to 40 percent shear deformation occurred, mainly on a single plane oriented at about 45 degrees to the tensile axis. The sample then fractured by decohesion along the same plane. In scanning electron microscope examinations of the morphology of the fractured surface, two regions were observed: a relatively featureless area corresponding to the region where plastic shear has occurred, and an area characterized by, in Leamy's words, "a river pattern of local necking protrusions" (Fig. 1) where the rupture occurred. This morphology is quite different from that occurring in crystalline metals, and one explanation is that, in localized high-stress regions, the amorphous metal is heated to a temperature above that of the glass transition and becomes much less viscous, enabling local plastic flow to occur and subsequently complete failure.

Similar studies of fracture in copper-zirconium alloys by R. Ray and B. C. Giessen at Northeastern University, Boston, Massachusetts, resulted in the observation of morphologies nearly identical to those in palladium-silicon. Thus, the same fracture mechanism may be common to all amorphous metals.

The large, localized shear deformation in palladium-silicon suggests the existence of dislocations, the line defect whose motion through crystalline materials is responsible for their relatively low strengths. Many scientists, including J. J. Gilman of Allied Chemical Corporation, believe that dislocation motion is a deformation mode in amorphous materials, and that the high strength of amorphous materials is due to the higher resistance to dislocation motion associated with the disordered structure of amorphous metals. J. C. M. Li of the University of Rochester, Rochester, New York, using a dislocation model for disordered materials, calculated that dislocation motion as a deformation mode required about half the stress that a uniform deformation would require and that this stress was close to experimentally observed shear stresses. He also noted that the definition of a dislocation as the boundary between deformed and undeformed (or more accurately between slipped and unslipped) regions in a metal is sufficiently general to apply to any kind of structure in which localized deformation could occur and is not restricted to crystals.

On the other side of the argument, Grant at MIT pointed out that he has never observed any plastic elongation in any of his copper-zirconium alloys and suggested that observation of such plastic deformation and of dislocation produced slip lines might be taken as evidence of microcrystallites rather than a random amorphous structure.

Not only are the mechanical properties of amorphous metals being extensively studied, but the magnetic properties of amorphous metals are attractive because of possible practical applications as well as for understanding the theory of disordered materials. The first prediction of ferromagnetism in disordered materials is widely attributed to A. I. Gubanov of the U.S.S.R. He showed that quantum mechanical exchange interactions between nearest magnetic neighbors in disordered structures could result in ferromagnetism. Shortly afterward, experimental confirmation of this prediction was made by several investigators in a variety of amorphous alloys.

### Amorphous Bubbles

The magnetic alloys of the most current interest are those usable in magnetic bubble domain devices. Previously, bubble domain materials have been crystalline thin films that have their magnetization oriented preferentially either up or down, perpendicularly to the plane of the film. They can be used as memory and storage devices in computers by controlling the generation and motion of "bubbles"—circular regions whose magnetization is oriented oppositely to that of the rest of the film. This year, Chaudhari and his co-workers at IBM's Thomas J. Watson Research Center announced the production, by sputtering, of amorphous antiferromagnetic gadolinium-cobalt and gadolinium-iron alloys that also exhibited the required perpendicular orientation of the magnetization. Chaudhari thinks that sputtered atoms arriving at the substrate surface move to certain energetically favorable sites and in this way build up a preferred orientation that otherwise would not be expected for the isotropic DRP structure.

Bubble domain devices also make use of another magnetic property that is characteristic of amorphous magnets —the magnetic softness—so that amorphous materials are both easily magnetized and demagnetized with only a low applied field, a necessity for rapid writing and erasing of bits of information in a computer memory or storage device. Chaudhari further noted that the wide range of compositions obtainable in amorphous alloys produced by sputtering provides a degree of tunability of the properties of the alloy. For example, most amorphous magnets have a lower Curie temperature than the corresponding crystalline alloy of the same composition. Recently, however, workers at IBM have produced a gadolinium-cobalt alloy with a higher Curie temperature by adjusting the alloy composition.

Efforts are being made to obtain a basic understanding of the nature of magnetism in amorphous materials. Mössbauer effect measurements provide a means of studying the local environment of atoms in both magnetic and nonmagnetic amorphous alloys and were first used by C. C. Tsuei and co-workers in the amorphous alloys group at Caltech (Tsuei is now working at IBM) to study magnetic iron-phosphorus-carbon alloys. According to Giessen at Northeastern University, who has reported Mössbauer studies with the iron-57 isotope in copper-zirconium alloys, the multiplicity of different local anisotropic environments tends to smear out the details of the Mössbauer spectra and thus far has prevented the elucidation of the details of the local structure. Magnetization and electrical resistivity as a function of temperature and neutron scattering are among other techniques used to unravel the magnetic structure of amorphous alloys.

Amorphous metallic alloys have other properties that may find practical application in specialized situations. As just one example, workers at both Bell Telephone Laboratories and Allied Chemical Corporation are interested in the ultrasonic attenuation properties of palladium-silicon alloys. It is believed that the low attenuation of the amplitude of acoustic waves in passing through these alloys may find application in a number of acoustic devices, such as delay lines in microwave signal processing circuits.

The field of amorphous metallic alloys has now entered the stage where an acceleration of scientific interest in the properties of disordered solids combined with the possibility of imminent commercial exploitation has conferred an aura of respectability to what was once a "far out" laboratory curiosity. While it seems clear that the level of interest in the scientific community will remain high for some time to come, it remains to be seen to what extent practical applications will follow.

—ARTHUR L. ROBINSON