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THE FOURTH INTERNATIONAL CONFERENCE ON LIQUID AND AMORPHOUS METALS: A TRIP REPORT

Although insulating glasses have been known since antiquity, metallic glasses (amorphous metals) are of a much more recent vintage, having been first fabricated in 1960 by Duwez and his co-workers[1] at the California Institute of Technology. Around the same period, Prof. R. B. Pond of The Johns Hopkins University patented a process for the fabrication of amorphous metals.[2] The fabrication method is actually quite simple and involves quenching liquids at rates exceeding a million degrees celsius per second.

Initially, metallic glasses were only of academic interest, allowing the possibility for studying the effect of topological and chemical disorder on the properties of metals. But soon after their introduction, the recognition of their attractive mechanical, magnetic, and corrosion properties – coupled with advances in production techniques – occasioned a veritable revolution in metallurgy. To discuss recent advances in the field, over 400 delegates from 26 countries gathered in Grenoble, France, for the Fourth International Conference on Liquid and Amorphous Metals, July 7-11, 1980. The conference was organized by the International Union of Pure and Applied Physics, the European Physical Society, a number of French scientific organizations, and several industrial groups. The previous three international conferences, held in 1966 at Brookhaven, 1972 at Tokyo, and 1976 at Bristol, were devoted exclusively to liquid metals, but that subject was overwhelmed at Grenoble by the recent surge of interest in amorphous metals.

Approximately one-third of the attendees were from the host nation, while the next largest delegation (about 50 persons) came from the Federal Republic of Germany, followed by 35 each from the United Kingdom and the United States, about 25 from Japan, 15 from Switzerland, and approximately 10 each from the German Democratic Republic, Italy, the Netherlands, and Sweden. Sixteen other countries were represented by one to seven delegates.

The scientific program consisted of 17 invited lectures delivered during the mornings, 236 contributed papers arranged in 18 poster sessions held during early afternoons, and six round-table discussion sessions during late afternoons. Papers on amorphous metals outnumbered those on liquid metals in both invited and contributed categories; out of 17 invited lectures, only four dealt exclusively with liquid metals, another three were concerned with both amorphous and liquid metals, and the other 10 dealt exclusively with amorphous metals. My interest is mainly in amorphous solids, particularly in their magnetic behavior; therefore, highlights concerning related topics will be emphasized in this report.

Atomic structures of amorphous solids can be specified with much less precision than those of their crystalline counterparts. The X-ray diffraction techniques only lead to a probabilistic distribution function for atomic positions in an amorphous solid that can be satisfied by several structural models. Early models for the atomic arrangements in metallic glasses were variations on a model based on random packing of hard spheres that was first introduced by Bernal to describe the structure of liquids. Such models inherently contain topological short-range order but, when extended to alloys, lead to random arrangement of various types of atoms. Until recently, such models enjoyed a fair degree of success, essentially because of the paucity of structural information apart from that obtained from X-ray diffraction techniques. But additional information obtained from neutron scattering on magnetic transition metal-metalloid (TM-Me) alloys indicated the presence of chemical short-range order. For example, no phosphorus atoms were found to be nearest neighbor pairs in an amorphous cobalt-phosphorus ($Co_{81}P_{19}$) alloy. At the conference, a large number of papers presented data not only from X-ray and neutron scattering techniques but also from extended X-ray absorption fine structure (EXAFS), nuclear magnetic resonance (NMR), and optical methods that support chemical short-range ordering at least in TM-Me alloys. In fact, NMR data showed that a number of amorphous molybdenum-boron, nickel-phosphorus-boron, and lanthanum-gallium alloys ($Mo_{70}B_{30}$, $Ni_{78}P_{14}B_8$, and $La_{75}Ga_{25}$, respectively) possess chemical ordering similar to that present in crystalline materials with similar composition.

An alternative approach to the study of the structure of amorphous solids is by computer modeling or simulation. An interesting paper at the conference presented the possibility of describing the short-range local structure and of testing such a description on a computer model. This allows computation of quantities such as stress tensor on an

atomic level. It is possible to identify regions of 10 to 20 atoms, each with either compressive or tensile hydrostatic stresses. It was shown that these regions occur often in pairs, with areas of high shear stresses between them. Physically, such regions represent volumes of different densities and can be identified formally with structural defects.

Neutron-scattering experiments on amorphous iron-boron (a-$Fe_{80}B_{20}$) also indicated the presence of local defects of approximate linear dimension of 1.5 nm and extended defects approximately 40 to 60 nm in size. The concept of a defect in an amorphous solid is intriguing though not widely accepted, and much quantitative work will have to be conducted before a consensus evolves.

Another aspect connected with inhomogeneity concerned simultaneous scattering and transmission Mössbauer spectroscopy of amorphous ribbons of iron-nickel-phosphorus-boron ($Fe_{40}Ni_{40}P_{14}B_6$). This provided a convenient and effective method of delineating differences between bulk and surface magnetic phenomena. It was reported that the average hyperfine field on the surface was approximately 7% larger than in the bulk, and the difference persisted on annealing. Also, the magnetic moments on the surface were found to be more aligned in the plane of the ribbon than those in the bulk. However, annealing decreased this difference.

Earlier models of stability and charge transfer effects in amorphous alloys have also been refined. A number of papers showed that in addition to the charge transfer, chemical bonding and atomic sizes play important roles in determining the properties of metal-metalloid alloys. For example, Group Four elements (carbon, silicon, germanium) were shown to have dramatically different effects on the magnetic moments of TM-Me alloys. Considering that the outer electron configuration and bonding of these elements are the same, the effect would not be understood without taking into account the different sizes of the three elements. Optical data on similar materials also emphasized the important contribution of hybridization between s-p electrons of the metalloid and d electrons of the transition metal.

The first glassy ferromagnet (Fe-P-C) was discovered in 1968.[3] Since then, many investigators have concentrated on magnetic aspects of amorphous TM-Me alloys. Such studies, in addition to elucidating magnetic phenomena, have contributed importantly to the study of structure in metallic glasses. The papers at the conference reflected the fascination for magnetic phenomena in amorphous metals. Considering that the formation of magnetic moments and exchange interactions between them continue to be elusive problems in crystalline solids, dealing with the added difficulties of disorder may indeed seem a folly. However, it is expected that the possibility of continuous changes in composition of amorphous alloys will shed light on the fundamentals of magnetic phenomena.

An interesting paper reflecting such a hope con-

cerned the Mössbauer study of amorphous cobalt-tin (Co_xSn_{100-x}), which was found to be ferromagnetic for $x \geq 50\%$. This is an intriguing result, considering that equilibrium phases of cobalt-tin do not exhibit ordered magnetic structure. It was proposed that the results can be understood in terms of the development of a magnetic moment on a cobalt atom only when it is surrounded by a rather large number (about eight or nine) of cobalt atoms, a condition not fulfilled in crystalline cobalt-tin alloys.

A number of presentations dealt with amorphous TM-Me alloys that contained approximately 80% iron or cobalt and therefore were ferromagnetic, but in which the magnetic order could be drastically modified when the above transition metal atoms were replaced by nickel, manganese, or chromium. Such a substitution led to the presence of both ferromagnetic and antiferromagnetic interactions, leading to "frustration" and the spin glass state at low temperatures where each spin freezes in a preferred direction that is randomly oriented and that is different for every spin (Fig. 1). Our presentation, "Spin Glass-Paramagnetic Phase Boundary in Amorphous Magnetic Alloys,"[4] showed that, while the presence of the spin glass phase depends on the relative concentration of two types of interactions, the details of the phase boundaries were determined by the relative strengths of the interactions. The predicted trends
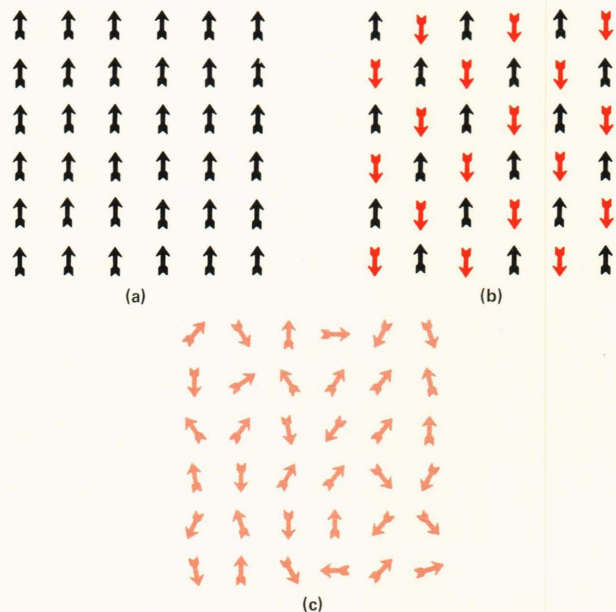

Fig. 1—Schematic representation of the ground state for (a) a ferromagnet, (b) a simple antiferromagnet, and (c) a spin glass. For a ferromagnet, all spins point in the same direction, while a simple antiferromagnet consists of two interpenetrating ferromagnetic lattices with spins on one lattice pointing in a direction opposite to that of the spins on the other lattice. Both ferromagnetic and antiferromagnetic states possess long-range order. The spin-glass state (c) exhibits no such long-range order and the spins point in random directions. The spin glass state differs from the paramagnetic state in that the directions of spins are "frozen."

were indeed observed in the amorphous magnetic alloys, $(Fe_xNi_{1-x})_{75}G_{25}$, $(Fe_xMn_{1-x})_{75}$ G_{25}, and $(Co_xMn_{1-x})_{75}$ G_{25}, where $G_{25} \equiv P_{16}B_6Al_3$, obtained by melt-quenching at Bell Telephone Laboratories and investigated at the University of Illinois by AC susceptibility techniques. A number of experimental papers confirming the presence of spin glass behavior in similar systems with different compositional content were presented.

Properties of a new class of metal-metal amorphous alloys, $(Fe-TM)_{90}Zr_{10}$ (where TM is vanadium, chromium, manganese, cobalt, or nickel), were presented at the conference. These materials differed considerably from the alloys where the glass-forming atoms were metalloids. Iron-zirconium $(Fe_{90}Zr_{10})$ was the first alloy containing such a large percentage of iron that was amorphous at room temperature. Its anomalously low value (1.29 μ_B/Fe atom) for the magnetic moment increased as other TM metals with fewer or more d electrons than iron were substituted for iron atoms. The value of the moment did reach a maximum; its value and the concentration at which it is attained depended on the substituted TM atom. Similar behavior was observed for the Curie temperature. These observations, combined with accurate density measurements, led authors to hypothesize that amorphous iron-zirconium $(Fe_{90}Zr_{10})$ contains ferromagnetically and antiferromagnetically coupled iron pairs, and replacing iron by the TM metals causes subtle changes in the iron-iron distances that suppress enough antiferromagnetically coupled pairs to cause an increase in moments as well as in Curie temperatures. It was further reported that quaternary alloys in the series $(Fe, Co, Ni)_{90}Zr_{10}$ with about 75 atomic percent of iron possess Invar characteristics in a wide temperature and composition range.

Although earlier studies had already indicated the importance of amorphous metals as highly corrosion-resistant materials, evidence that corrosion resistance is not ubiquitous in amorphous metals was presented at the conference, and the potential and limitations were better defined. For example, iron-, cobalt-, or nickel-based glasses were found to be less stable than their crystalline counterparts, but the use of copper to partially replace iron in iron-phosphorus glasses dramatically improved corrosion resistance. The corrosion resistance was also shown to depend on metalloid content and to increase with increasing valence of the metalloid. The superior corrosion resistance of particular alloys was attributed to the microscopic chemical and physical homogeneity of the surface of these alloys and to the rapid formation of highly protective passive surface films because of the high concentration of metalloid elements. The important aspect is that the surface activity of amorphous metals differs considerably from that of crystalline metals, and it is susceptible to large changes when the composition is changed.

The potential applications of metallic glasses are indeed wide-ranging, from use in power devices (such as distribution transformers and motors) to electronic devices (such as continuously variable surface-acoustic-wave delay lines or resonators, magnetic shielding, and recording heads). Core losses as a function of induction are substantially less in amorphous $Fe_{80}B_{20}$ than in the conventional Fe-3.2% Si-grain-oriented sheet steel. It is estimated that if all power distribution transformers in the United States were replaced by amorphous metallic transformers, power losses could be reduced by 60%. The outstanding performance of a number of laboratory devices gives confidence in their future use in industry.

Overall, the conference was extremely well organized, not only scientifically but also socially. The round-table discussions at the end of each day proved to be excellent forums for crystallizing controversial points that otherwise were a little too amorphous.

REFERENCES and NOTES

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