## Research News

# Aluminum-rich Metallic Glasses

An enormous variety of metallic liquid solutions have been converted by rapid quenching from the melt into metallic glasses. They fall into two large groupings: (1) M + m, where M is a metal and m a metalloid, and (2) M + M', where only metals are present. In both categories, one or both M's most commonly are transition metals. Group-1 glasses often contain two or more distinct metalloids, whereas up to now studies of group-2 glasses have been restricted to binary systems. The total solute content has rarely been less than 15 at.%, and ≈20 at.% is more common.

Of the many hundreds of alloy systems in which melt-quenched metallic glasses have been recorded since the sport was invented in 1959, none include aluminum, although a few instances have been recorded of *partial* vitrification of rapidly quenched aluminum melts containing Si, Ge, Cu, Ni, Cr or Pd as solute—i.e., a small amount of glassy phase coexisted with a larger amount of metastable crystalline phase. Aluminum has always been regarded as a solvent inimical to glass formation.

It is therefore an occasion for surprise that within a few months, two teams in different countries, working quite independently of each other, have discovered similar families of aluminum-rich alloys that can be completely vitrified by rapid quenching from the melt. *Inoue, Ohtera, Tsai* and *Masumoto* in Sendai, Japan, were the first to publish;[1] they were followed five months later by *He, Poon* and *Shiflet*[2] in Charlottesville, Virginia. Both teams used single-roller melt-spinning (the most usual method used for research purposes nowadays): in this technique, a jet of molten alloy is directed at an angle at the circumference of a rapidly spinning copper wheel, and a narrow quenched ribbon is generated. In thework discussed here, the ribbons were 15–30 μm thick and 1–2 mm wide.

The two groups both made glasses always containing *two* solutes, one being a rare earth metal and the other a transition metal. The Japanese effort was entirely concentrated on the Al-Y-Ni system: the investigators found that *both* solutes were necessary to make a glass. Figure 1 shows the range of compositions in this system which gave fully amorphous ribbons: one Al-Y-Ni alloy examined by the American investigators is also included in this figure (in the lower left part). The Americans also studied a variety of other ternary aluminum alloys, in all of which the solutes were combinations of a rare earth and a transition metal. these included individual compositions in the Al-Ce-Fe, Al-Gd-Fe, Al-Ce-Ni, Al-Ce-Co, Al-Y-Co, Al-Ce-Rh and Al-Y-Ni systems. All of these had total solute contents of only 10–13 at.%, and it is noteworthy that the most interesting mechanical properties in the American study were found for the most dilute alloy, $Al_{90}Ce_5Fe_5$.

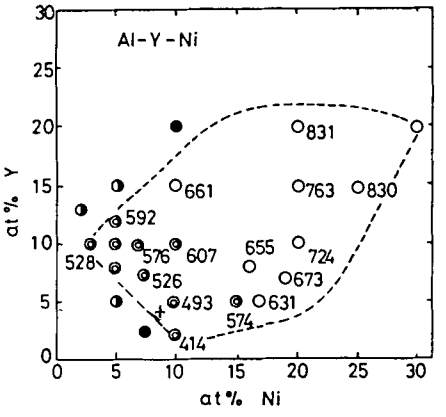


Fig. 1. Compositional range of melt-spun Al-Y-Ni alloys: ◎ amorphous, ductile; ○ amorphous, brittle; ◑ amorphous plus crystalline; ● crystalline. The numbers give the crystallization temperatures [°C] (from reference [1]). The cross in the lower left part gives a composition of an amorphous Al-Y-Ni alloy found by *He* et al. [2].

None of the numerous theoretical criteria which have been proposed to interpret glass-forming ability (GFA) of different alloy combinations and compositions[3] will help us here: for some of them (e.g., a criterion based upon the volume change on melting) we lack the experimental information that would enable us to check their applicability; for others we are faced by the difficulty that the criteria are applicable only to binary alloys. However, a very recent study[4] from the Virginia group, on Al-Fe-Gd glasses, has established that there is no deep eutectic anywhere in the glass-forming region and that the reduced glass-forming temperatures, $T_r > T_x/T_m$ (where $T_x$, $T_m$ are crystallization and melting temperatures, respectively) are abnormally high (0.65–0.70); the reason is unknown. High $T_r$ always favors glass formation, but the normal route to a high $T_r$ is via depression of $T_m$ at deep eutectics. These glasses, therefore, are anomalous.

The most thoroughly researched criterion for high GFA is undoubtedly the degree of mismatch in atomic size between solvent andsolute, and this criterion also appears to have the widest applicability.[3] For binary alloys, this criterion was studied in great detail by *Egami* and *Waseda*,[5] who established a functional relationship between the disparity in atomic volumes and the minimum solute concentration needed for a glass to be made in that alloy system: the larger the disparity, the smaller the minimum solute concentration needed. This quantified the well established

principle that crystallization of a melt is inhibited if it contains atoms differing widely in size.

*Egami* and *Waseda*'s analysis is not directly applicable to ternary alloys, but it is interesting to note that the rare earth solute atoms are always larger than the aluminum solvent, while the transition metal atoms are smaller. By way of example, atomic volumes for two of the new aluminum glasses (in $Å^3$) are: Al 16.6, Ce 34.4, Fe 11.8;—,Y 33.0, Ni 10.9. The implication is that a mixture of small and large solute atoms is particularly favorable for stabilizing a liquid/amorphous structure and discouraging crystallization. This conclusion is consistent with one of the few earlier studies that looked systematically at ternary glasses: *Ohnuma* et al.[6] examined a range of Co-B-TM alloys, where various transition metals were partially substituted for boron. It was found that the total solute content needed to achieve vitrification was the smaller, the larger the size of the transition metal atom: in general, the larger the disparity between the size of the solvent (cobalt) atom and the sizes of the (larger) transition metal and (smaller) boron solutes, the easier it was to make a glass.

The practical interest of the new glasses lies in their strength. *He* et al. found tensile strengths in the range 670–940 MPa, while *Inoue* et al. reported values in the range 730–1140 MPa for various compositions in their single alloy system. These strengths greatly exceed the strengths of even the best precipitation-hardened crystalline aluminum alloys (300–500 MPa) and the possibility of using ribbons of some of the new alloys as reinforcing fibers in composites at once presents itself. Advantages include in particular the low density of the fibers, their ductility which offers the prospect of enhanced intrinsic ductility in composites incorporating them, as well as good corrosion resistance. Drawbacks include a relatively low Young's modulus (up to 71 GPa), somewhat lower than for crystalline aluminum alloys, and rather low crystallization temperatures, 250–370 °C for the compositions of greatest interest. However, this is still higher than the limiting temperature of use for organic fibers such as Kevlar.—The *Wall Street Journal* for October 6 carried a report of an interview with a staff scientist of Allied-Signal Corporation which is the principal commercial manufacturer of metallic glasses. This scientist very reasonably doubted whether the new glasses could be used as massive constructional materials, but made no reference to use in composites. The Virginia authors, also interviewed, expressed the belief that the aluminum glasses have a rosy future in the aerospace industry.

Research on metallic glasses, which excited a steadily high level of interest during the 1970s and early 1980s,[7] has shown signs of abating recently. Perhaps the new aluminum glasses will inject a new vitality into this field: certainly many questions related to the formation, properties and crystallization of these glasses deserve to be addressed.

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## Conference Reports

# High-Temperature Superconductors in Strasbourg ...

The symposium on preparation and applications of high-temperature superconductors at the European Materials Research Society (E-MRS) conference on November 8–10, 1988 in Strasbourg, France attracted more than 200 scientists from Europe and overseas. Thirty-eight lectures, 15 of which were invited, and over 100 posters were presented in ten sessions. Most presentations discussed the structure of $YBa_2Cu_3O_7$ and Bi- and Tl-based superconductors, including the effect of substitutions and impurities. Other areas of interest were the preparation and characterization of thin film superconductors as well as bulk and thin film properties and their measurement by a variety of techniques such as X-ray photoelectron spectroscopy, Raman spectroscopy, nuclear magnetic resonance, etc. In addition, practical applications such as a Meissner-Ochsenfeld motor constructed by AEG engineers were presented during one of the two poster sessions.

A new phase in the Y-Ba-Cu-O system, namely $Y_2Ba_4Cu_8O_{16}$, which was reported at the Interlaken meeting earlier this year to be present in some thin films, can