Bulk Amorphous Metal— An Emerging Engineering Material

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During the last two decades, researchers have developed families of metal alloys that exhibit exceptional resistance to crystallization in the undercooled liquid state. Upon cooling, these alloys readily form glass or vitrify to form bulk amorphous alloys or bulk metallic glasses. The stability of the undercooled molten alloys with respect to crystallization has enabled studies of liquid thermodynamics, rheology, atomic diffusion, and the glass transition previously not possible in metallic systems. Bulk amorphous alloys exhibit very high strength, specific strength, and elastic strain limit, along with unusual combinations of other engineering properties. These factors, taken together, suggest that bulk amorphous metals will become widely used engineering materials during the next decade.

INTRODUCTION

The vitrification of a liquid metal alloy was first reported in the Au-Si alloy system in 1959 by Duwez et al.[1] in their pioneering studies of rapid solidification technology (RST). In these early experiments, liquid alloys were spread in thin layers on a conductive substrate to achieve cooling rates of 10^5–10^6 K/s. The application of RST methods to liquid alloys later led to numerous binary and ternary glass-forming alloys and to the development of a commercial planar flow casting technology[2] for production of continuously cast ribbons and thin sheets of amorphous metal. Engineering interest during the 1970s and 1980s focused mainly on soft magnetic properties of these materials and applications as transformer cores and magnetic devices. Early indications that metallic glass could be formed at much lower cooling rates (~1,000 K/s) were reported in the 1970s beginning with Chen[3], who demonstrated casting of millimeter diameter rods of Pd-Cu-Si alloys using a suction casting method. In 1982, Lee et al. reported millimeter diameter spheres of Au-Pb-Sb glass produced by cooling in a drop tower.[4] In 1982–1983,[5] using fluxing methods, the Turnbull group at Harvard succeeded in forming ~1 cm vitrified ingots of a Pd-Ni-P alloy at cooling rates well below 100 K/s. The Turnbull group noted that these alloys had a reduced glass-transition temperature, $t_g = T_g/T_L \approx 2/3$, similar to silicate glasses. Here, T_g is the glass-transition temperature (in K) and T_L is the alloy-melting temperature, m, or, more rigorously, the liquidus temperature.

Beginning in about 1989, the Inoue group in Sendai, Japan, carried out systematic studies of glass formation in a variety of multicomponent alloys using variable cooling rates obtained by casting rods and strips of varying thickness into metal molds.[6,7] They reported bulk glass formation of millimeter to centimeter thick samples in several families of alloys. These included magnesium-based, lanthanum-based, and zirconium-based alloys at cooling rates below ~100 K/s.[7] This was followed, in 1993, by glass formation in complex Zr-Ti-based beryllium-bearing alloys[8] at directly measured cooling rates of 1 K/s reported by Peker et al.[9] It was shown that these glasses could be cast into amorphous rods up to at least several centimeters in diameter, and that the onset of crystal nucleation at any temperature in the undercooled liquid range was independent of sample size and required elapsed process times of ~1 minute or more.[9]

During the past decade, the number of papers appearing in the literature dealing with bulk amorphous alloys has grown steadily. Recent meetings and conferences on the topic reveal an ever-increasing list of alloy compositions that form bulk glasses of millimeter or greater thickness. Bulk amorphous alloy formation, defined in terms of the ability to cast glasses several millimeters thick, appears to be relatively ubiquitous in higher-order alloy systems. Further

Table I. Characteristic Properties of Bulk Glass-Forming Metallic Liquids

Liquid Alloy Properties	Role in Bulk Glass Formation
Low Alloy Liquidus Temperature and High Reduced Glass-Transition Temperature, $t_g = T_g/T_L \approx 0.58 - 0.67$	Reduced thermodynamic driving force for crystallization at a given rheological temperature, T/T_g
Strong Liquid Behavior, – Viscosity falls slowly with T/T_g – Relatively high viscosity at T_L (3–4 orders of magnitude greater than elemental liquids)	– Reduced atomic mobility in the temperature range $T_g < T < T_L$ – Viscosity ~ 10 Pa-s at T_L – Suppressed crystal nucleation and growth
Liquid/Liquid Phase Separation – Liquid miscibility gap between T_g and T_L	– Crystal nucleation and growth is often preceded by liquid-phase separation – Liquid-phase separation becomes the rate-limiting step in crystallization – Glass formation optimized when miscibility gaps are avoided