

A highly processable metallic glass: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$

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We report on the properties of one example of a new family of metallic alloys which exhibit excellent glass forming ability. The critical cooling rate to retain the glassy phase is of the order of 10 K/s or less. Large samples in the form of rods ranging up to 14 mm in diameter have been prepared by casting in silica containers. The undercooled liquid alloy has been studied over a wide range of temperatures between the glass transition temperature and the thermodynamic melting point of the equilibrium crystalline alloy using scanning calorimetry. Crystallization of the material has been studied. Some characteristic properties of the new material are presented. The origins of exceptional glass forming ability of these new alloys are discussed.

Since the first report of metallic glass formation by rapid solidification of liquid metallic alloys,¹ there has been extensive effort to develop metallic alloys which exhibit high resistance to crystallization in the undercooled liquid state. Using rapid solidification methods such as splat quenching, melt spinning, etc., with characteristic cooling rates in the range of 10^3 – 10^6 K/s, it has been found that many binary and ternary alloys form metallic glasses. The classical theory of nucleation and growth of crystalline phases in an undercooled melt has been used by Turnbull² to account for the glass forming ability of these materials. Among the alloys studied, several ternary noble metal alloys systems such as Pd-Cu-Si,³ Au-Pb-Sb,⁴ and Pd-Ni-P,^{3,5} have been observed to exhibit glass formation at cooling rates 10^3 K/s or less. Recently, the group of Masumoto and Inoue have reported several new families of glass forming alloys such as La-Al-Ni,⁶ Zr-Ni-Cu-Al,⁷ and Mg-Cu-Y,⁸ which require very low cooling rates for glass formation. Samples of these alloys having a smallest dimension ranging up to several millimeters have been obtained. For example, fully glassy rods with diameters as large as 7–8 mm have been obtained by casting of the latter two types of alloys in copper molds. Upon heating above the glass transition temperature in a scanning calorimeter, the undercooled melt has been found to remain free of crystal nucleation up to temperatures more than 100 K in excess of the glass transition temperature. As such, these glassy alloys can be processed in the undercooled liquid state during laboratory time scales. In the present letter, we report on the formation and properties of a pentiary glass forming alloy which is representative of a new family of glass forming alloys currently under study in our laboratory. The alloy forms glass at cooling rates of less than 10 K/s. Large fully amorphous rods up to 14 mm in diameter have been prepared by melting in silica tubes and quenching in water. The alloy is highly processable in the undercooled liquid regime.

Mixtures of elements of purity ranging from 99.5% to 99.9% and having the nominal composition $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ were alloyed by induction melting on a water cooled silver boat under a Ti-gettered argon atmosphere. Ingots of typical size of 5–6 g were prepared. The initial samples were generally found to

freeze without any crystallization during preparation resulting in a glassy ingot. Typical examples of glassy ingots are shown in Fig. 1. The ingot samples were further processed by casting into copper molds under an inert gas atmosphere and by melting of several ingots together in sealed silica tubes followed by water quenching. Silica tubes ranging from 6 to 14 mm in diameter were used. Uniform plates, strips, and bars, as well as rods were made by these methods in a variety of shapes and sizes. Several examples are shown in Fig. 1. X-ray diffraction patterns were obtained with an Inel position sensitive detector using Co $K\alpha$ radiation ($\lambda=0.1790$ nm). Thermal analysis was carried out using a Perkin-Elmer DSC 4 scanning calorimeter interfaced to a personal computer for data processing and analysis. The samples were contained in aluminum pans and scanned in a flowing argon atmosphere. To determine the crystalline alloy melting point, a Seteram DSC 2000 K high temperature calorimeter was used in the DSC mode.

The samples shown in Fig. 1 include rectangular bars and plates prepared by casting in copper molds. The figure shows both a top view and cross-sectional view. The two

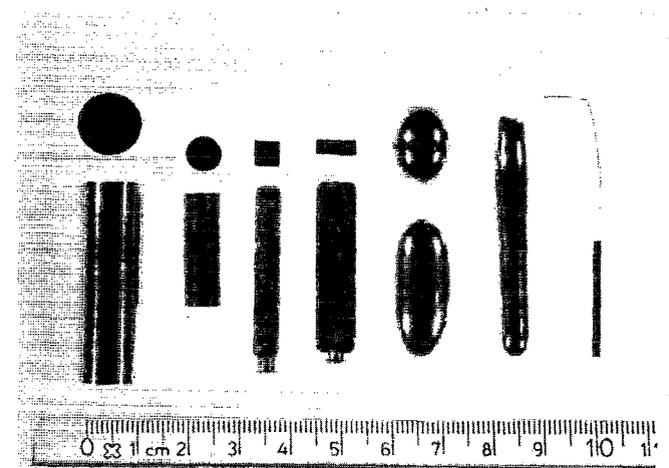


FIG. 1. Samples of glassy alloy prepared by various processes. From left to right: 12.6-mm-diam rod and its cross section, 7.0-mm-diam rod and its cross section, 5×5 mm bar and its cross section, 3×8 mm plate and its cross section, 2 oval shape ingots of 9 g each, barlike ingot of 8 g, and 1.5-mm-thick strip and its final form after rolling down to 15- μ m-thick ribbon.

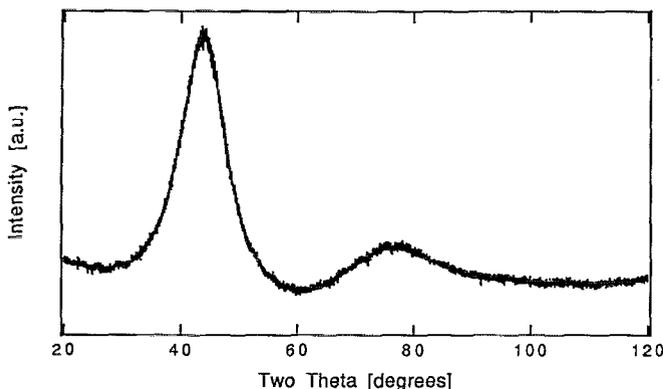


FIG. 2. X-ray diffraction pattern (CoK α radiation) taken from the cross-sectional surface of 12.6-mm-diam rod obtained by water quenching in a silica tube.

rods (7 and 12.6 mm) were prepared by water quenching in silica tubes. X-ray diffraction patterns were obtained from the outer surfaces as well as on various cross-sectioned surfaces of the samples. No evidence of crystallization is found in any of the x-ray patterns. Figure 2 shows a typical x-ray pattern taken from the cross-sectional surface of the 12.6 mm rod obtained by water quenching in a silica tube. The sample is completely amorphous. A 14 mm sample showed similar results. We have not as yet established an upper bound on the rod diameter which can be quenched to the glassy state.

Vicker's hardness measurements on these samples show a typical value of 585 kg/mm². The glassy alloy is very ductile at ambient temperature when deformed under confined geometries. For example, a plate with 1.5 mm thickness was cold rolled at ambient temperature down to a 15 μ m thick ribbon without crack formation. The final ribbon can still sustain a 90° bend as seen in Fig. 1.

Figure 3 shows DSC scans of the glassy alloy using a heating rate of 20 and 200 K/min. In the 20 K/min scan, a heat capacity anomaly characteristic of the glass transition can be seen beginning at 625 K with a heat capacity

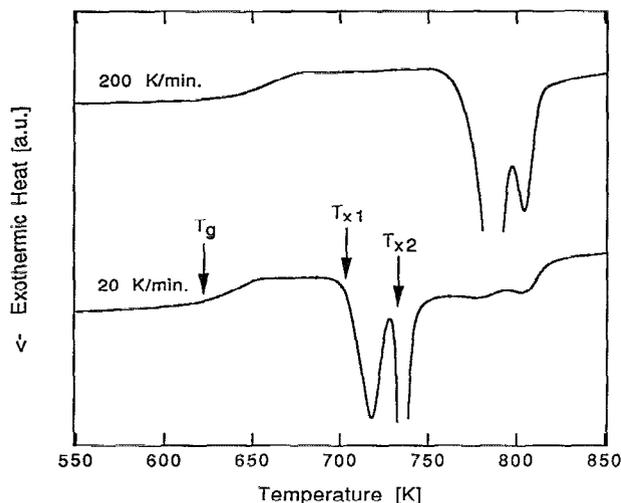


FIG. 3. DSC scans at 20 and 200 K/min of glassy alloy.

maximum at slightly higher temperature. At higher temperatures, two crystallization events are seen. The onset of the first occurs at 705 K while the onset of the second is at 735 K. The location of both peaks depends strongly on the rate of heating as can be seen by comparison with the DSC scan at higher heating rate. Other factors have also been found to strongly influence crystallization behavior. For example, the development of surface oxide has been observed above 675 K in samples scanned in flowing argon. Such oxidation can be suppressed by fluxing the sample surface with a layer of borosilicate glass or encapsulation in a thin glass ampoule. When this is done, surface oxidation is suppressed and contact with the aluminum pan is prevented. Under these conditions, the crystallization peaks move to higher temperatures.⁹ More detailed results of this type will be discussed in another publication.

The reduced glass transition temperature, $t_g = T_g/T_m$ (where T_g is the calorimetrically defined glass transition temperature and T_m is the alloy melting point) has often cited in the literature^{2,10} as a critical parameter which determines the glass forming ability of metallic alloys. High values of t_g are associated with glass forming ability. For example, the Pd-Ni-P alloys mentioned above have $t_g = 0.66$,^{5,10} while for the Au-Pb-Sb alloys $t_g = 0.63$.⁴ Melting studies of the present alloy using Seteram DSC 3000 K gives a solidus temperature of 937 ± 3 K and liquids temperature of 993 ± 5 K. We believe the solidus temperature to be a eutectic temperature. From the comparison of endothermic signals of the solidus and liquidus line, we can deduce that the alloy is very close to a eutectic composition. Taking $T_g = 625$ K and $T_m = 937$ K (the eutectic temperature), we obtain $t_g = 0.67$ for the eutectic alloy, which should have comparable or possibly better glass forming ability. This is among the highest values of t_g reported for metallic alloys so far and is consistent with the exceptional glass forming ability of the material.

To explain the exceptional glass forming ability of these alloys, both thermodynamic and kinetic factors must be taken into account. The large values of t_g imply a small relative temperature range over which nucleation and growth of crystals can occur. From our DSC studies, we estimated the total entropy of fusion, ΔS_f of these alloys to be approximately 6.6 J/mol K. Using the Turnbull approximation² for the free energy difference between the liquid and crystalline phases in the undercooled regime,

$$\Delta G_{xl} = \Delta S_f(T_m - T) + \text{higher order terms,}$$

gives a very small driving force for crystallization. The higher order terms involve the heat capacity difference between the liquid and crystal and generally reduce the driving force for crystallization relative to the first term. For example, at 780 K (at lower temperatures, kinetic freezing of the melt sets in), we estimate $\Delta G_{xl} = 1.0$ kJ/mol. This relatively small driving force for crystallization will tend to result in a relatively large nucleation barrier for crystals in the restricted undercooled region. A second factor which may influence crystallization is the complexity of the five component alloy. We note, for example, that the atomic radii of the elemental constituents vary over a large range.

The atomic radius of Be is 0.111 nm, those of Ni and Cu are 0.124 and 0.128 nm, while those of Zr and Ti are 0.160 and 0.147. These differing sizes are expected to limit the solubilities of these elements in crystalline phases having a small number of nonequivalent positions in the unit cell, thus requiring large chemical fluctuations to form critical nuclei of the crystalline phases. In support of this argument, we note that Tanner has studied glass formation by rapid quenching in Zr-Be and Ti-Be alloys.¹¹ In the Ti-Be system, glass formation is pre-empted by formation of a metastable CsCl-type structure near the equiatomic composition. Nucleation of this metastable phase is suppressed when Zr is substituted for Ti in the alloys. Apparently, the larger atomic diameter of Zr limits its solubility in the CsCl-type phase and makes nucleation of this phase more difficult in the ternary alloys. Masumoto and Inoue^{7,12} have suggested that atomic size differences in multicomponent alloys lead to efficient packing of atoms in the glassy phase. This in turn leads to a smaller ground state energy difference between the amorphous and crystalline phases. This small difference together with the lowering of the free energy of the liquid due to chemical mixing entropy effects

can be related to the existence of deep eutectic structures such as found in our alloys. We will report the glass forming range of the Zr-Ti-Cu-Ni-Be system elsewhere.

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