Thermal and elastic properties of Cu–Zr–Be bulk metallic glass forming alloys

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The compositional dependence of thermal and elastic properties of Cu–Zr–Be ternary bulk metallic glass forming alloys was systematically studied. There exists a linear relationship between the glass transition temperature T_g and the total Zr concentration. G decreases linearly with increasing Zr concentration as well. The results also show that T_g, shear modulus G, and Poisson's ratio ν are very sensitive to changes in compositions. Low T_g, low G, and relatively high ν can be achieved with high Zr and Ti concentration. © *2007 American Institute of Physics.*
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Bulk metallic glasses (BMGs) have acquired significant attention from scientific and technological view points in the past 20 years.[1,2] BMGs usually show high strength, high specific strength, large elastic strain limit, and excellent wear and corrosion resistances along with other remarkable engineering properties. Researchers have developed families of binary and multicomponent systems[3–11] to form BMGs, among which Zr-based Be-bearing BMGs (Vitreloy series)[3] have been utilized commercially to produce items including sporting goods and electronic casings.

The glass forming ability (GFA), and rheological and mechanical properties of different alloy systems have been extensively studied. Previous literature indicates that highly processable Vitreloy BMGs tend to show rather strong liquid behaviors.[12–14] Recently, it was discovered that Cu–Zr binary alloys,[7,10,15] which can be cast into bulk amorphous structures with sample diameters up to 2 mm, show relatively fragile behaviors in viscosity.[16] Therefore, it is believed that there exists a balance point between GFA and fragility, which can be utilized to design novel bulk amorphous alloy systems.

There is plenty of evidence to show that the ductile behavior of BMGs is closely related to their Poisson's ratio.[17] For instance, the Pt-based BMG (Ref. 18) with high Poisson's ratio of ~0.41 shows excellent compressive ductility and high fracture toughness, while the Fe-based BMG with low Poisson's ratio of ~0.30 (Ref. 19) shows poor ductility and low fracture toughness. It was also reported that the critical Poisson's ratio[19] for compressive plasticity in Fe–Mo–C–B–Ln BMGs is about 0.32, where an onset of plasticity was observed. Novikov and Sokolov[20,21] found that Poisson's ratio of a glass at room temperature correlated well with the fragility of glass forming liquids at high temperature. In an effort to further understand the relationship among Possion's ratio, fragility, and GFA, we report in this letter, the compositional dependence of thermal and elastic properties in Cu–Zr–Be bulk metallic glass forming alloys.

Conner and Johnson reported[22] that the bending ductility of amorphous alloys in the Zr–Ti–Ni–Cu–Be system is composition dependent. Alloys with a higher Zr:Ti ratio show better ductility over a wide range of compositions than those with a lower Zr:Ti ratio. It is empirically known as well that Ni rather makes the glass forming liquid stronger thus resulting in better GFA. Therefore, by eliminating Ni and Ti from Vitreloy series, we carried out systematic studies on bulk glass formation, and thermal and elastic properties in the Cu–Zr–Be alloy system. According to our design, it is believed that the Cu–Zr–Be glassy alloys have higher Poisson's ratio and lower shear modulus, while maintaining the good processability of Be-bearing BMGs.

Mixtures of elements of purity ranging from 99.9% to 99.99% were alloyed by induction melting on a water cooled silver boat or arc melting under a Ti-gettered argon atmosphere. Ingots of typical size of 10 g were prepared. Each ingot was flipped over and remelted at least three times in order to obtain chemical homogeneity. The ingots then were remelted under high vacuum in a quartz tube using an induction heating coil and injected through an ~0.5–1 mm (inner diameter) nozzle into copper molds using high-purity argon at a pressure of ~1–2 atm. These copper molds have internal cylindrical cavities of diameters ranging from 1 to 10 mm. A Philips X'Pert Pro x-ray diffractometer and a Netzsch 404C differential scanning calorimeter (performed at a constant heating rate 0.33 K/s) were utilized to confirm the amorphous nature and to examine the thermal behaviors of these cast samples. The pulse-echo overlap technique with 25 MHz piezoelectric transducers was used to measure the shear and longitudinal wave speeds at room temperature for each of the samples. Sample density was measured by the Archimedean technique according to the American Society of Testing Materials standard C 693-93. To get rid of any possibility of cooling effect on the elastic properties,[23–25] we carried out the measurements on 2.5 mm cast strip samples for all the alloys studied in this letter.

The glass forming ability in the Cu–Zr–Be ternary alloy system was systematically studied. Considering that the total Zr and Ti concentration in Vitreloy 1 is 55%, the Zr content in Cu–Zr–Be alloys studied was chosen to range from 50% to 65%, while the Be varies from 16% to 30%. Figure 1 shows bulk glass formation diagram in this ternary system. The amorphous nature of all the samples studied in this work has been confirmed by x-ray diffraction and thermal analysis. The best GFA region is found when the Zr concentration is

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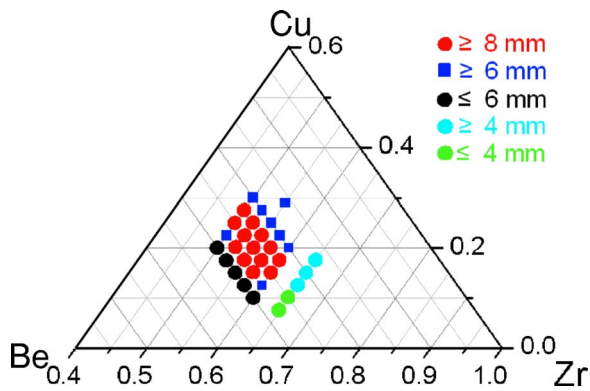[a]Author to whom correspondence should be addressed; electronic mail: duan@caltech.edu.

FIG. 1. (Color online) Bulk metallic glass formation map in the Cu–Zr–Be ternary alloy system.
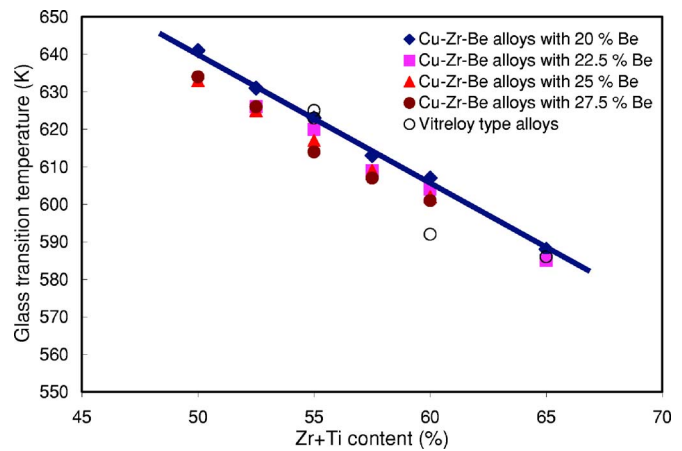

FIG. 2. (Color online) Glass transition temperature as a function of the total Zr and Ti content in Cu–Zr–Be ternary and Vitreloy-type bulk metallic glasses.

between 50% and 60%. The alloys can be cast into fully amorphous rods of diameter at least 8 mm provided that Be is between 22.5% and 27.5%. When Be is reduced to less than 20%, 6 mm fully amorphous rods could still be obtained by copper mold casting. However, once Be is greater than 30%, the GFA is observed to decrease to below 6 mm. If Zr is increased to be 65% in the Cu–Zr–Be ternary system, the casting diameter of fully amorphous rods is limited to about 4 mm or below.

A summary of the thermal and elastic properties of the representative glassy alloys in the Cu–Zr–Be ternary system and Vitreloy-type BMGs (Refs. 26 and 27) is listed in Table I. The variations of supercooled liquid region ΔT ($\Delta T = T_x - T_g$, in which T_x is the onset temperature of the first crystallization event and T_g is the glass transition temperature) and reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_l$, where T_l is the liquidus temperature) are calculated. It is clearly seen from Table I that T_{rg} follows a decreasing trend with increasing Zr concentration in Cu–Zr–Be ternary system, which is consistent with Fig. 1. We also note that all the ternary alloys show very good thermal stability. For example, $Zr_{55}Cu_{20}Be_{25}$, $Zr_{57.5}Cu_{17.5}Be_{25}$, and $Zr_{60}Cu_{17.5}Be_{22.5}$ show large supercooled liquid regions of over 100 K. When compared to Vitreloy 1 and Vitreloy 4, Cu–Zr–Be ternary alloys are designed to have higher Poisson's ratios and lower shear moduli by removing Ni and Ti and sacrificing some of the GFA.

The glass transition temperatures of Cu–Zr–Be ternary alloys and Vitreloy-type alloys as a function of the total concentration of Zr and Ti are plotted in Fig. 2. It is noticed that there exists a linear relationship between T_g and Zr(Ti) con-

centration. Small variations may occur depending on the Be content. T_g is high at low Zr(Ti) concentrations (640 K for $Zr_{50}Cu_{30}Be_{20}$), decreasing to 607 K ($Zr_{60}Cu_{20}Be_{20}$) and to 588 K as Zr(Ti) content increases to 65% ($Zr_{65}Cu_{15}Be_{20}$). The slope was measured to be -3.5 K per 1% change in Zr(Ti) concentration. We also note that $Zr_{65}Cu_{12.5}Be_{22.5}$ shows a T_g of 585 K, which is 38 K lower than that of Vitreloy 1.

We present the shear modulus G as a function of Zr(Ti) concentration and the Poisson's ratio ν as a function of Zr(Ti) concentration in Figs. 3 and 4, respectively. It is shown that both G and ν are very sensitive to changes in composition. $Zr_{50}Cu_{30}Be_{20}$ exhibits a high G of 36.4 GPa, and increasing Zr in Cu–Zr–Be alloys decreases G, which drops to 27.3 GPa for $Zr_{65}Cu_{15}Be_{20}$. The line in Fig. 3 represents the best linear fit to the data obtained from Cu–Zr–Be alloys with Be concentration of 20%. The slope was measured to be -0.6 GPa per 1% change in Zr content. As indicated in Table I, the bulk modulus B of all the Cu–Zr–Be ternary alloys and Vitreloy series does not change much and remains nearly constant at $\sim$110 GPa. The open circles in Figs. 3 and 4 depict the effects of Ni and Ti on G as well as on ν for Vitreloy-type alloys. Apparently, designing novel BMGs with high Poisson's ratios and lower shear moduli by removing Ni and Ti is confirmed since Ni and Ti increase G remarkably and therefore reduce ν. The highest ν that we can achieve from Cu–Zr–Be ternary alloys is 0.386 for $Zr_{65}Cu_{12.5}Be_{22.5}$, which has a G of 27.5 GPa.

TABLE I. Thermal and elastic properties of representative Cu–Zr–Be and Vitreloy-type glassy alloys.

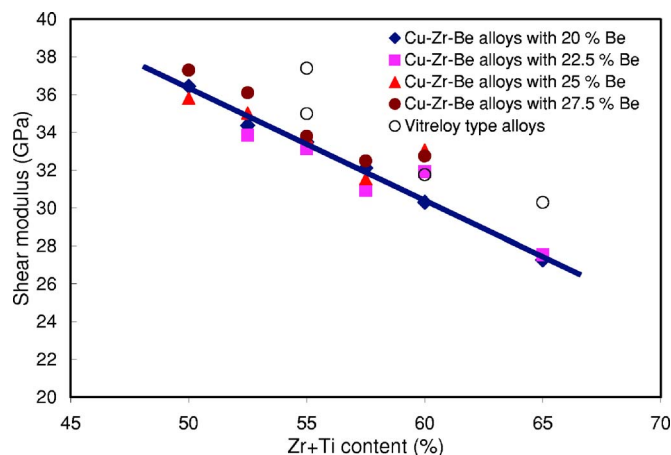| Materials	T_g (K)	T_x (K)	T_l (K)	ΔT (K)	T_g/T_l	G (GPa)	B (GPa)	Y (GPa)	ν
$Zr_{50}Cu_{25}Be_{25}$	633	721	1140	88	0.555	35.8	108.9	96.8	0.35
$Zr_{52.5}Cu_{22.5}Be_{25}$	625	715	1124	90	0.556	35.0	111.5	92.0	0.36
$Zr_{55}Cu_{20}Be_{25}$	617	720	1122	103	0.550	33.7	108.1	91.6	0.36
$Zr_{57.5}Cu_{17.5}Be_{25}$	609	715	1109	106	0.549	31.5	105.1	85.9	0.36
$Zr_{60}Cu_{17.5}Be_{22.5}$	604	707	1110	103	0.544	31.9	111.2	87.3	0.37
$Zr_{65}Cu_{12.5}Be_{22.5}$	585	684	1098	99	0.533	27.5	111.9	76.3	0.39
$Zr_{51}Ti_9Cu_{15}Be_{25}$	592	$\cdots$	1047	$\cdots$	0.565	31.8	104.3	86.5	0.36
$Zr_{54}Ti_{11}Cu_{12.5}Be_{22.5}$	586	$\cdots$	1035	$\cdots$	0.566	30.3	103.5	82.8	0.37
$Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$	623	712	993	89	0.627	37.4	115.9	101.3	0.35
$Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$	625	738	1185	113	0.527	35.0	110.3	95.0	0.36

FIG. 3. (Color online) Shear modulus G vs. the total concentration of zirconium and titanium in Cu–Zr–Be ternary glassy alloys and Vitreloy-type bulk glassy alloys.

Recently, a cooperative shear model has been developed for the glassy state based on potential energy landscape/inherent state theory to describe the yielding behavior in metallic glasses.[26] A scaling relationship among the shear flow barrier, a universal critical yield strain, and the isoconfigurational shear modulus G was constructed. The model reveals that for a fixed glass configuration the barrier height for shear flow is proportional to the isoconfigurational shear modulus G, which makes G of great importance to fully understand the mechanical behaviors of BMGs and to design novel BMGs. In the Cu–Zr–Be ternary system, the bulk modulus B remains almost constant. Therefore, lower G implies higher Poisson's ratio and means that the shear flow barrier for an

unstressed shear cooperative zone is relatively small. This allows the atoms to get into a higher potential energy configuration, which would benefit the yielding behaviors.[23]

In summary, we designed a class of Cu–Zr–Be BMGs with rather high Possion's ratios compared to Vitreloy series by removing Ni and Ti. The compositional dependence of thermal and elastic properties was systematically studied. The results show that T_g, G, and ν are very sensitive to changes in compositions. Low T_g, low G, and relatively high ν can be achieved with high Zr(Ti) concentration, which helps to design bulk glassy alloys and composites.
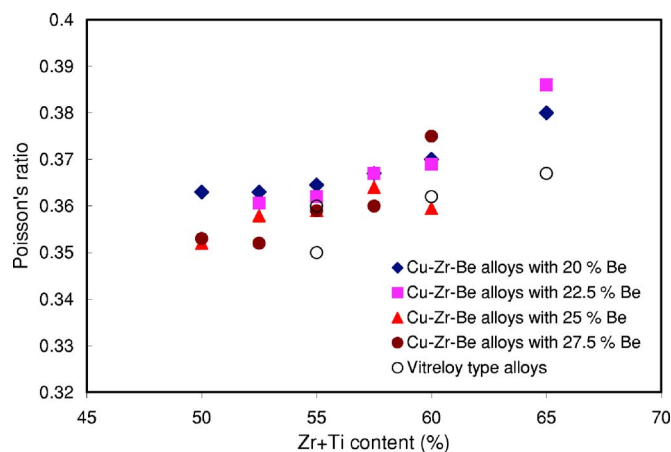
FIG. 4. (Color online) Poisson's ratio as a function of the total Zr and Ti concentration in Cu–Zr–Be ternary glassy alloys and Vitreloy-type bulk amorphous alloys.

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