

# Characteristics of microstructure and glass transition of $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$ bulk metallic glasses

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The glass transition and the microstructural characteristics of  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  ( $10 \leq x \leq 16$ ) bulk metallic glasses (BMG) are investigated as function of Al content. It is found that the Al content has strong effects on the glass transition, microstructure, and properties of the alloy. The marked increase of the Debye temperature and shear modulus with increasing Al content indicates that the different Al incorporations result in microstructural change in atomic short range of the BMG. The increase of the glass transition temperature with the increase Al content is consistent with the large variation of properties with increase of Al content. The change of the microstructure of the glass-forming alloy is responsible for the change of the properties. © 2003 American Institute of Physics. [DOI: 10.1063/1.1526153]

The recent discovery of bulk metallic glasses (BMGs) is significant for both fundamental and practical reasons.<sup>1-5</sup> Zr-Ti-Cu-Ni-Al bulk metallic glass-forming alloys belong to the new families of BMGs that have been found to exhibit exceptional glass-forming ability (GFA) and unique physical properties. However, the formation mechanism of glass and the glass transition are still a physical challenge.<sup>6</sup> The excellent GFA of an alloy is usually explained by the confused principle.<sup>7</sup> However, it is found that the GFA is also strongly dependent on some constituents. In Zr-Ti-Cu-Ni-Al alloys; Al and Ti play a critical role in the formation of the BMG,<sup>8</sup> but not much information exists on the effects of Al on the microstructure and the properties of the BMG. Acoustic properties are particularly sensitive to the microstructure of a solid, and the BMG is in a suitable form for measurements of elastic wave propagation. The structure and properties as well as the relation between them for the BMG can be investigated by the ultrasonic method.<sup>9-11</sup> The determination of the acoustic velocities with the change of Al incorporation can provide useful information on the microstructural characteristics of the BMG. In this letter, the effects of Al incorporation (Al content varies from 10 to 16 at. %) on the microstructure, glass transition, and properties of the  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  alloys were investigated by acoustic and density measurements, x-ray diffraction (XRD), and differential scanning calorimetry (DSC). It is found that a slight change in Al incorporation results in local structural change, which results in a much higher glass transition temperature, a denser atomic packing, and a marked increase of shear modulus and Debye temperature of the BMG.

$(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  ( $10 \leq x \leq 16$ ) BMGs were prepared by arc-melting a mixture of pure metals in purified argon atmosphere, that is then sucked directly into a water-cooled copper mold to form cylinders of 5 mm in diameter and 80 mm in length. The amorphous nature as well

as the homogeneity of the rod was ascertained with XRD and high-resolution transmission electron microscopy.<sup>12</sup> XRD measurements were performed using a Siemens D5000 diffractometer with  $\text{Cu K}\alpha$  radiation. Thermal properties were studied by DSC performed in a Perkin-Elmer DSC-7 under flowing purified argon at a heating rate of 10 K/min. The density  $\rho$  was measured by the Archimedian principle. Ultrasonic measurement was carried out in a MATEC 6600 ultrasonic system with a 10 MHz frequency and a measuring sensitivity is 0.5 ns. The details about the experiments are given in Ref. 9. The shear modulus  $G$  and the Debye temperature  $\theta_D$  can be calculated from the longitudinal velocity  $v_l$  and transverse velocity  $v_s$ .<sup>11</sup>

Figure 1 shows the XRD curves obtained from the cross-section slice cut from the middle part of cylinder of the as-cast  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  ( $x = 10, 12, 14.3, \text{ and } 16$ ) alloys. The broad and diffuse diffraction maxima without sharp crystalline diffraction peaks indicate that the alloys are almost single amorphous phase. Figure 2 presents the corresponding DSC traces of the  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  BMGs. All the DSC traces exhibit the obvious endothermic characteristic of a glass transition followed by an exothermic crystallization peak. The glass transition temperature  $T_g$ , and crystallization temperature  $T_x$  of the BMGs increase from 657 to 697 K, 751 to 793 K with Al increasing from 10 to 16 at. %, respectively. This demonstrates that the thermal stability of the BMG is improved with increasing Al content. A large supercooled liquid region,  $\Delta T_x$  ( $\Delta T_x = T_x - T_g$ ) is found for these BMGs, and the values of  $\Delta T_x$  are all above 85 K. An unusual phenomenon is that  $T_g$  increases by 40 K for 6 at. % Al variation. In general,  $T_g$  is not sensitive to the composition change of an alloy; for example,  $T_g$  shows only minor difference with composition change for the ZrTiCu-NiBe BMG.<sup>13</sup> It might be expected that the increase  $T_g$  mainly resulting from the addition of Al is due to the different binding strength of Zr(Ti)-Cu(Ni) and Zr(Ti)-Al, which is represented by the more negative heat of mixing of Zr-Al ( $-45$  kJ/mol) compared to Zr-Cu ( $-24$  kJ/mol).<sup>14</sup> The

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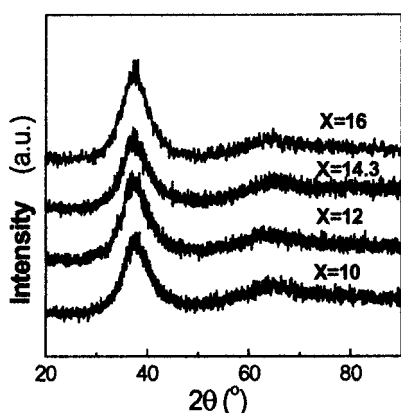


FIG. 1. The XRD patterns of as-cast  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  alloys.

change of the atomic configuration on a short-range scale originates mainly from the change in the chemical short-range order by the dissolution of Al. The other effect of Al on the thermal stability is the effect of atomic size, in which the addition of the middle atomic size of Al in Zr–Ti–Cu–Ni–Al alloys leads to an increase of the packing density in the amorphous solid and in the supercooled liquid.<sup>15</sup>

The density and the acoustic velocities were measured to study the microstructural change with increasing Al content. The values of  $\rho$ ,  $v_l$ , and  $v_s$  of the BMGs are listed in Table I. The number of the atoms in unit volume  $n$  can be calculated by  $n = \rho/A$ , where  $A$  is the average atomic weight. The  $G$  and  $\theta_D$  values, which can provide important information about the microstructural characteristics of a solid, are determined by acoustic measurements. The relative change of  $\Delta Y/Y_0 = (Y - Y_0)/Y_0$  ( $Y = n, G, \theta_D, T_g$ ;  $Y_0$  is a normal value for the BMG with 10 at. % of Al) is shown in Fig. 3.  $n$ ,  $G$ ,  $\theta_D$ , and  $T_g$  monotonically increase with increasing Al content. It can be clearly seen from Fig. 3 that a small increase of  $n$  leads to larger relative changes of  $G$ ,  $\theta_D$ , and  $T_g$ . The relative increase of  $n$  is 1.4% when Al content increases from 10 to 16 at. %. The increase means that the atomic packing becomes denser with increasing Al content in the BMG. The relative increase of  $G$  and  $\theta_D$  when Al content increases to 16 at. % are 12.4% and 6.4%, respectively. In comparison,

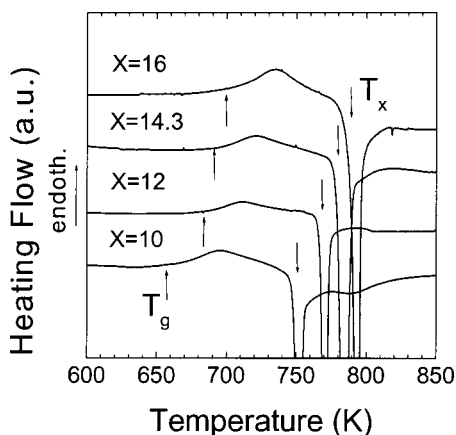


FIG. 2. DSC curves of the  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  BMG with a heating rate of 10 K/min.

TABLE I. The thermal parameters obtained by DSC at a heating rate of 10 K/min and properties for as-cast  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  BMGs.

Al content at. %	$T_g$ (K)	$T_x$ (K)	$v_l$ (km/s)	$v_s$ (km/s)	$\rho$ (g/cm <sup>3</sup> )	$n \times 10^{-2}$ (mol/cm <sup>3</sup> )	$\theta_D$ (K)	$G$ (GPa)
10	657	751	4.777	2.155	6.749	9.22	278.9	31.3
12	681	770	4.825	2.232	6.696	9.29	287.8	33.4
14.3	689	786	4.890	2.269	6.593	9.30	290.9	33.9
16	697	793	4.845	2.319	6.553	9.35	296.4	35.2

the relative changes of  $G$  and  $\theta_D$  for the  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{90}\text{Al}_{10}$  BMG corresponding to its fully crystallized state (annealed at 873 K for 1 h) are only 7% and 2.5%, respectively, even though the relative change of  $n$  (1.45%) between the glassy and crystallized states is similar to that induced by Al incorporation. Al, like Be in the ZrTiCuNiBe glass-forming alloy system,<sup>13</sup> plays an important role in the formation of the BMG. Like Al, Be has a large negative heat of mixing with Zr (−69 kJ/mol) and Ti (−48 kJ/mol).<sup>14</sup> However, the change of Be content in ZrTiCuNiBe BMGs does not significantly change the glass transition,  $G$  and  $\theta_D$ .<sup>10,12</sup> The present result indicates that more and more Al incorporation results in a very large change of properties, and the average atomic strength of the alloys with higher Al content is greatly enhanced.<sup>11</sup>

To make clear what factors lead to the large change of the  $G$  and  $\theta_D$ , the acoustic velocities of the  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{85.7}\text{Al}_{14.3}$  BMG were measured *in situ* under applied pressure. The corresponding pressure dependences of  $G$ ,  $\theta_D$ , and  $n$  of the BMG are shown in Fig. 4. The investigation shows that  $G$  and  $\theta_D$  increase with the increase in atomic packing density resulting from pressure, but the relative changes of  $G$  and  $\theta_D$  corresponding to 0.4% change of  $n$  are only about 1.2% and 0.5%, respectively. Comparing the BMGs with increasing Al content from 14.3% to 16% (the change of  $n$  is 0.5%), the relative changes of  $G$  (3.8%) and  $\theta_D$  (1.9%) are much larger than that resulting from pressure with similar  $n$  variation. The results indicate that the increased  $G$  and  $\theta_D$  induced by the incorpora-

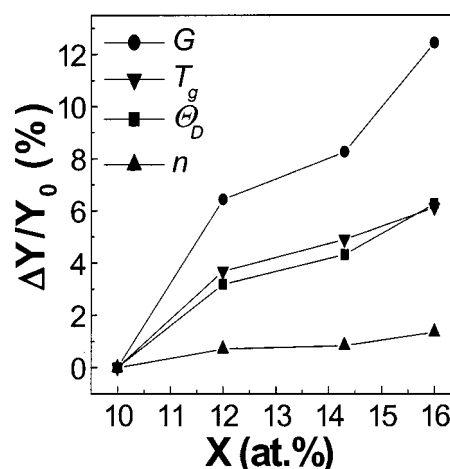


FIG. 3. The relative change of  $\Delta Y/Y_0 = (Y - Y_0)/Y_0$  ( $Y = n, G, \theta_D, T_g$ ;  $Y_0$  is a normal value for the BMG with 10 at. % of Al) upon Al content for the  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$  BMG.

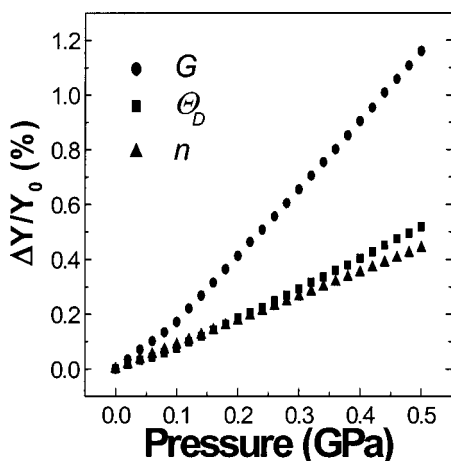


FIG. 4. The relative change of  $\Delta Y/Y_0 = (Y - Y_0)/Y_0$  ( $Y = n, G, \theta_D$ ,  $Y_0$  is a normal value for the BMG at ambient pressure) upon pressure for the  $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{86.7}\text{Al}_{14.3}$  BMG.

tion of Al are not mainly attributed to the large change of the atomic packing density. It is well-known that a softening effect exists when an alloy is formed into amorphous state.<sup>16,17</sup> The softening effect is due to the absence of long-range order in metallic glasses, and the interaction of the atoms is restricted to short-range order effects.<sup>18</sup> Correspondingly, the very large change of properties resulting from the already small changes in the Al content is relative to the change of microstructure in the short-range. However, due to the multicomponents, small size, and random orientation of the short-range order (or building block) of the amorphous alloy, what kind of microstructural change occurs has remained experimentally inaccessible, and can be determined only by indirect evidence.

The change of  $T_g$  with the increase of Al content in the BMG has a correlation with  $\theta_D$ , as shown in Fig. 3. The glass transition is evidently associated with a certain density of packing of the atoms and the energy state associated with this packing.<sup>19</sup> The phonon-phonon interactions in metallic glass become dominant near  $\theta_D$ , and cooperative phonon interactions generate sufficient local energy to allow atoms to cross the barrier-saddle energy, preventing their translational motions from becoming possible. The saddle energy is related to the short-range structure.<sup>20</sup> In most cases  $T_g$  is not equal to  $\theta_D$ , indicating that the saddle energy is mostly higher than the energy of the atom at  $\theta_D$ . In Zr-Ti-Cu-Ni-Al BMGs,  $T_g$  is much larger than  $\theta_D$ . Our experimental results

indicate that the increase in Al content stabilizes the short-range structure more than the density of the atomic packing. Hence, the higher increases the value of  $\theta_D$  resulting from the slighter Al content. Accordingly, the energy needed to change the energy state is larger, and the glass transition shifts to higher temperatures with increasing Al content.

In conclusion, the glass transition, thermal stability, the Debye temperature, and shear modulus of ZrTiCuNiAl BMGs exhibit marked changes with small changes in the Al content. The results indicate that the microstructure in the short-range of the BMG is very sensitive to the Al content. A slightly higher Al content results in the microstructural change, which leads to a significantly higher glass transition temperature, a denser atomic packing, and a marked increase of the shear modulus and the Debye temperature of the BMG.

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