Glass Forming Ability and Mechanical Properties of Quinary Zr-Based Bulk Metallic Glasses

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Quinary Zr-based alloy compositions with improved glass forming criteria have been sought and the glass forming ability (GFA), thermal stability and mechanical properties of these alloys have been investigated. Monolithic amorphous structure has been confirmed for all compositions in 5 mm rods prepared by a Cu-mold casting method. They also show large plastic strain maximum of about 12% under uniaxial compression test with yield stress of about 2000 MPa. The compressive plasticity of the cast rods was found to be influenced by the casting temperature to a great extent. [doi:10.2320/matertrans.MF200621]

(Received January 9, 2007; Accepted April 17, 2007; Published May 25, 2007)

Keywords: metallic glass, plastic strain, shear band

1. Introduction

Recent research thrust in the field of BMG is to design glasses with better GFA and improved mechanical properties. During the last decade, numerous new multicomponent bulk amorphous alloys have been developed.1,2) These alloys have low critical cooling rates (~10 Ks⁻¹) and a fully amorphous structure in bulk rods with diameters as large as about 70 mm. A number of attempts have been made to understand the controlling factors on GFA in order to predict alloy compositions with larger dimensions. Jin et al.3) recently found the good glass forming composition of Zr₅₈Cu₂₂Fe₈Al₁₂ in the Zr-Cu-Fe-Al system.

In the present work, we report five quinary Zr-based metallic glasses derived from the Zr₅₈Cu₂₂Fe₈Al₁₂ alloy without degrading the glass forming ability of the parent alloy by minor addition of Co and Ag. All of these alloys were found to show good compressive strains of about 5–10% in compression. It has also been clearly shown for the first time that the cast temperature influences the plasticity value of BMG to a great extent.

2. Experimental Procedure

Zr₅₈Cu₂₂Fe₈Al₁₂, Zr₅₈Cu₂₂Co₄Fe₄Al₁₂, Zr₅₈Cu₃₅Cr₄Ag₁₂Al₁₂, Zr₅₈Cu₂₆Fe₄Ag₄Al₁₂, Zr₅₈Cu₂₆Co₂₆Ag₈Al₁₂ and Zr₅₈Cu₃₅Fe₂₄Ag₈Al₁₂ alloy ingots were prepared by arc melting high purity Zr (99.9%), Cu (99.99%), Ag (99.99%), Co (99.9%) and Al (99.9%) under Ar-atmosphere. 2–5 mm diameter rods of 50 mm length metallic glass samples were prepared using copper mold casting from the ingots in an Ar-atmosphere. The casting unit was equipped with a radiation temperature recorder. Melt temperatures before casting were varied from 1253 K to 1473 K for the Zr₅₈Cu₂₆Co₄Fe₄Al₁₂. All the other alloys were cast from 1253 K. The structure of the cast alloys was examined using x-ray diffraction (XRD) with monochromatic Cu-Kα radiation. Thermal analysis of as-cast samples was performed by a Perkin–Elmer Pyris 1 differential scanning calorimetry (DSC) at a heating rate of 40 K/min. Differential thermal analysis (DTA) of as cast alloys was performed by a Rigaku Thermoplus TG 8110 at a heating rate of 40 K/min to measure the liquidus temperatures. Compression tests were performed at a quasi-static strain rate of 1 × 10⁻⁴ s⁻¹ in an Instron machine using rod samples of 2 mm diameter and 4 mm length at room temperature. Fractographic analysis of mechanically tested samples was performed with scanning electron microscopy (SEM). Specimens for transmission electron microscopy (TEM) were prepared by mechanical grinding followed by ion milling using a Gatan Model 691 PIPS machine. Gentle milling was also carried out after milling in PIPS. TEM observation was carried out using a Philips CM200 TEM operating at 200 kV.

3. Results and Discussion

Figure 1(a) shows the XRD patterns of 5 mm rods of five alloys cast from 1253 K. XRD patterns indicate amorphous nature of the alloys. Figure 1(b) shows the XRD patterns of 2 mm diameter rods of the Zr₅₈Cu₂₆Co₄Fe₄Al₁₂ alloy that were cast from three different temperatures. XRD patterns indicate amorphous nature of the alloys. Figure 2(a) and (b) show TEM bright field images and selected area electron diffraction (SAED) patterns of the 5 mm diameter rods of Zr₅₈Cu₂₆Co₄Fe₄Al₁₂ and Zr₅₈Cu₂₆Fe₂₄Ag₈Al₁₂ alloys as representatives of all the five alloy compositions. For the both samples, TEM images are featureless and SAED patterns consist of a single halo ring without any diffraction spots. No crystalline phases are observed in Fig. 2, indicating that both the as-cast alloys are completely amorphous without any detectable heterogeneity. The other alloys also showed the same fully amorphous feature in TEM observations.

Figure 3 shows DSC traces of the 5 BMG samples measured at a heating rate of 40 K/min, which are characterized by the presence of clear glass transition temperature Tg (glass transition temperature) and one strong exothermic peak followed by another small crystallization peak. The crystallization sequences of the quinary alloys are similar to the one reported for the base quaternary alloy.3) There are large differences in Tc (crystallization onset temperature) values although Tg remains almost at the same level. Table 1 shows the thermal properties and GFA criteria of the six

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glassy alloys. All the derived quinary compositions have high values in different GFA criteria proposed by many investigators such as $T_{rg}$, $\Delta T_x$, $\gamma$ and $\alpha$ (5,6) ($\gamma = T_x/(T_g + T_l)$ and $\alpha = T_x/T_l$) compared to the quaternary alloy. Among the alloys, the Zr$_{58}$Cu$_{22}$Co$_4$Fe$_4$Al$_{12}$ alloy has a very wide supercooled temperature region of about 115 K and highest $\gamma$ and $\alpha$ values, which have been proven to be better GFA criteria than the reduced glass transition temperature ($T_{rg}$) (5,6), suggesting that this alloy can be cast into a larger diameter than the quaternary alloy.

Size differences between the three principal elements in the quinary alloys are around 12% or more (radius of Zr, Cu, Al, Fe, Co and Ag are 0.160, 0.128, 0.143, 0.124, 0.125 and 0.144 nm, respectively (7)). The enthalpies of mixing of three principal elements are also highly negative ($\Delta H_{mix}$ of Zr-Cu, Zr-Al, Zr-Fe, Zr-Co, Zr-Ag are −23, −44, −25, −41 and −20 kJ/mol, respectively (8)). Co has similar properties as Fe with almost the same atomic radius. On the other hand, Ag forms a eutectic with Al near Ag$_{40}$Al$_{60}$ composition. Replacement of Fe with Co and Ag was proved to be helpful in giving comparable GFA values with Zr$_{58}$Cu$_{22}$Fe$_8$Al$_{12}$ cited in Table 1 for the currently derived Zr-based quinary alloys. Complex intermetallic phases $\varepsilon$ and Al$_2$Co$_2$ form at Fe$_{40}$Al$_{60}$ and Co$_{40}$Al$_{60}$ compositions in their respective binary phase diagrams. It increases the complexity of the alloy and hinders crystallization. In the present alloy systems, as the amount Co or Fe % increases, there is increase in $T_x$ (Table 1). $T_x$ values of Zr$_{58}$Cu$_{22}$Fe$_2$Ag$_6$Al$_{12}$, Zr$_{58}$Cu$_{22}$Fe$_4$Ag$_2$Al$_{12}$ and Zr$_{58}$Cu$_{22}$Fe$_8$Ag$_6$Al$_{12}$ BMGs are 748, 757 and 761 K, respectively. Consequently, $\gamma$ and $\alpha$ values of the three alloys show increasing trend from 0.393 to 0.407 and 0.61 to 0.64, respectively with the increase in Fe content. On the other hand, $T_x$ of Zr$_{58}$Cu$_{22}$Co$_2$Ag$_6$Al$_{12}$ and Zr$_{58}$Cu$_{22}$Co$_4$Ag$_2$Al$_{12}$ BMGs are 751 and 761 K, respectively. Consequently, $\gamma$ and $\alpha$ of the above two alloys show increasing trend from 0.395 to 0.408 and 0.61 to 0.64, respectively with the increase in Co content. Zr$_{58}$Cu$_{22}$Fe$_4$Al$_{12}$ has the highest $T_x$ value of 788 K. This suggests that Co and Fe helps in improving the GFA of the alloys not because of forming eutectic with Al at 40:60 atom percentage, rather because of complex phase formation with Al in their respective phase diagram which finally helps in increasing $T_x$ values. However, formation of eutectic between Fe and Al has been considered to be the reason by Jin et al. (3) for the development of highly bulk forming glassy alloy.

The criteria for GFA, in particular $\gamma$, of the current alloys have also been found to have a good correlation with the values of enthalpy of mixing of amorphous ($\Delta H_{mix}^{amorph}$) of the alloys calculated by using Miedema model (9,10). $\Delta H_{mix}^{amorph}$ can be expressed as.
where, $x_i$ are molar concentrations of i-th element, $H_{i,\text{amorph}}$ is the enthalpy for amorphous pure metal ($H_{i,\text{amorph}} = \alpha T_{mi}$), where $\alpha = 3.51 \text{ mol/K}$ and $T_{mi}$ is the melting point of the i-th element. $\Delta H_{\text{Chem}}$ can be calculated using the formula given by Murty et al.\textsuperscript{10} and references therein. $\Delta H_{\text{Chem}}$ for binary alloys can be written as

$$\Delta H_{\text{Chem}} = x_i x_j (\Delta H_{\text{sol,i,j}} + x_i A_{i,\text{sol}} + x_j A_{j,\text{sol}} + x_i A_{i,j})$$

Where, $x_i$ and $x_j$ are the molar concentrations of components i and j, respectively. $\Delta H_{\text{sol,i,j}}$ can be obtained from the reference mentioned in Ref. 10. However, for amorphous phase, $\Delta H_{\text{Chem}}$ for AB binary is multiplied with the factor (1 + 5($x_A^2$ $x_B^2$)) for the account of short range order observed in amorphous phase. where, $x_A = \frac{x_A V_2/3}{x_A (V) 2/3}$, $x_B = 1 - x_A$. For the calculation of $\Delta H_{\text{Chem}}$ for multicomponent system containing more than 3 elements can be done following the way as shown by Rao et al.\textsuperscript{11}

$$\Delta H_{\text{Chem}} = \sum_{i,j}^N \Delta H_{\text{Chem}} A_i A_j$$

where i and j denote the components. A denotes the element name. N is the total number of components. The values of $\Delta H_{\text{mix,amorph}}$ calculated for the present alloys are shown in Table 1. An alloy having higher negative $\Delta H_{\text{mix,amorph}}$ would have a higher driving force for glass formation and hence, it enhances higher glass forming ability. All the quinary alloys have very high negative $\Delta H_{\text{mix,amorph}}$ values close to $-40 \text{ kJ/mol}$ and the Zr$_{58}$Cu$_{22}$Co$_4$Fe$_{4}$Al$_{12}$ alloy has the highest negative $\Delta H_{\text{mix,amorph}}$ of $-47 \text{ kJ/mol}$. The largest values $\Delta T_x$, $\gamma$, $\alpha$ and $\Delta H_{\text{mix,amorph}}$ of the Zr$_{58}$Cu$_{22}$Co$_4$Fe$_{4}$Al$_{12}$ alloy suggesting that this is the best alloy in terms of bulk formability. In fact, we have confirmed that at least 5 mm diameter rods can be cast as fully amorphous from the alloy, the diameter of which could go further if larger moulds can be used.

Figure 4 shows the nominal stress-strain curves obtained from uniaxial compression tests of all the six BMGs cast from 1253 K. All the quinary alloys show larger total compressive strain before fracture ($\varepsilon_t$) than the Zr$_{58}$Cu$_{22}$Fe$_2$Al$_{12}$ alloy. The Zr$_{58}$Cu$_{22}$Fe$_2$Ag$_6$Al$_{12}$ BMG has the highest $\varepsilon_t$ of about 11.5% which is relatively high value in comparison to a few highly ductile Zr-based BMGs (compressive strain is near about 10% or more) in literature.\textsuperscript{12-14} There are also reports on the improvement of plasticity on addition of elements having positive enthalphy of mixing ($\Delta H_{\text{mix}}$) with other elements.\textsuperscript{14-17} For examples, addition of Nb to Ni-based,\textsuperscript{15} Nb and Ag to Cu-based\textsuperscript{16,17} and Ta to Zr-based BMGs\textsuperscript{14} were reported to enhance the plasticity of the respective alloys. Choice of elements to improve the plasticity of the BMGs without loosing the glass forming ability has been guided by the concept of addition of elements having positive enthalphy of mixing. In the present alloy systems, the addition of elements having positive $\Delta H_{\text{mix}}$ with Cu leads to enhanced plasticity ($\Delta H_{\text{mix}}$ of Cu-Co, Fe-Cu and Cu-Ag are 10, 19 and 2 kJ/mol, respectively)\textsuperscript{8}). However, Fig. 4 indicates that the enhancement of plastic strain is more pronounced with the combination of Co and Ag or Fe and Ag. $\Delta H_{\text{mix}}$ values of Fe-Ag and Co-Ag are 42 and 28 kJ/mol,
The addition of the alloying element having positive heat of mixing with constituent elements may provide atomic-scale local chemical inhomogeneity or fluctuation in local free volume distribution, thereby affecting the propagation behavior of the shear bands.

In previous reports, many discussions on the plastic strains depending on alloy compositions have been made. However, no work has reported that the plastic strain is actually very sensitive to the casting conditions. The compressive stress-strain curves for the Zr$_{58}$Cu$_{22}$Co$_4$Fe$_4$Al$_{12}$ 2 mm rods that were cast from various melt temperatures are shown in Fig. 5. The Zr$_{58}$Cu$_{22}$Co$_4$Fe$_4$Al$_{12}$ alloy was chosen as it has the highest GFA criteria and the lowest strain among all the five quinary alloys. The samples that were cast from higher temperatures show higher strain values of about 13–15%. At intermediate cast temperature (1323 K), the alloy shows the highest strain (15%).

Factors which can govern plasticity of cast BMG from the processing point of view are annealing near $T_g$, melt temperature and cooling rate employed during casting. It has already been shown that annealing near $T_g$ makes the BMG brittle due to the loss of free volume. Thus, the nanocrystal/amorphous composite structure that is formed by annealing does not usually enhance the plasticity. However, if nanocrystal/amorphous composite is formed during solidification, it can lead to enhancement of the plasticity values of the plastic strain as reported in Cu-Zr-Ti BMG. Melt temperature is also very much important as shown in Fig. 8. There are reports that the same BMG studied by different research groups gives different plasticity values. For example, Cu$_{50}$Zr$_{50}$ shows more than 50% plasticity in one case where injection casting has been employed. The same composition gives only 8% strain in another case where suction casting has been used. Recent report also has suggested that even if the same injection casting is used, still there would be wide difference in the plasticity values of the Cu$_{50}$Zr$_{50}$ metallic glass due to inherent change in the structure. This could be either due to difference in cooling rate or difference in melt temperature which definitely change the structure of the glassy phase which, in turn, leads to such a wide difference in plasticity in Cu$_{50}$Zr$_{50}$ system.

However, in the present context, how the cast temperature changes the structure of the Zr$_{58}$Cu$_{22}$Co$_4$Fe$_4$Al$_{12}$ alloy as indicated by the change in the DSC traces (Fig. 6) and TEM images shown in Fig. 7. Strong dependency of plasticity on melt temperature has also been observed in the other four quinary BMGs. Hence, it can also be concluded that not only the composition of BMGs, but also cast temperature and cooling rate should be considered while discussing the plasticity of cast BMG.

4. Conclusions

(1) Five quinary alloys with improved GFA have been derived from the Zr-Cu-Fe-Al metallic glass. They can be cast at least 5 mm diameter fully amorphous rod.

(2) These alloys exhibit plastic strains of about 12% in compression.
It has also been shown clearly that the change in the process parameters such as casting temperature has a great effect on the compressive plasticity in bulk metallic glass. The sample that showed large plastic strain were partially crystallized during solidification. When discussing the amount of plastic strains of BMGs, processing conditions should be considered.

Acknowledgment

This work was supported by the grant-in-aid of scientific research, Priority Area “Science of Metallic Glass” of MEXT, Japan. The authors thank Dr. G. Kumar for his discussion and help in the experiments.

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