1. Introduction

Bulk metallic glasses (BMGs) have been developed in many alloy systems in the last decade.1) Due to their prominent mechanical properties, BMGs have been considered as the promising materials for industrial application. Recently, much attention was paid for Cu-based BMGs because they have higher strength and lower price as compared with Zr-base BMGs. For the Cu-Zr-Ti, 2) Cu-Zr-Al, 3) and Cu-Hf-Ti 4) alloy systems, high GFA has been reported. Moreover, it was shown that the addition of Be, Y and Sn improved the GFA of the Cu-Zr-Ti ternary alloys; and the maximum diameter reached 5 mm for the as-cast glassy rods.5–7) Based on the results of the Cu-Zr-Al ternary alloys, 5) Xu et al.8) have found that Cu_{60}Zr_{20}Al_{12}Y_{5} alloy can be solidified into a fully glassy structure with a diameter of 10 mm. More recently, it was found that binary Cu-Zr alloys can form BMGs in a wide range of compositions, 9–11) though their BMGs usually include nanocrystalline particles and their critical diameter is limited up to 2 mm. It was later shown that addition of Al or Ag elements improved the GFA of the Cu_{50}Zr_{50} alloy. 12,13) It is an interesting work to develop CuZr-based BMGs with larger sizes. One simple method for developing the unknown multicomponent bulk metallic glass-forming alloys is to use equiatomic substitution on the basis of well known glass alloy compositions.14) By applying equiatomic substitution derived from the three empirical rules for BMG formation, 1) we present different type of Cu-Zr-based quaternary BMGs with the composition (Cu_{0.5}Zr_{0.5})_{100-x}-(Ti_{x}Al_{1-x})_x, where x = 0, 4, 6, 8, 10, 12. Quaternary Cu-Zr-Ti-Al alloys exhibit high GFA, and the maximum critical diameter reaches 7 mm. Since the compositions studied here are free from Ni and they exhibit high strength, the quaternary Cu-Zr-Ti-Al bulk metallic glasses may be also useful in biomedical application.

2. Experimental Procedure

The sponge Zirconium and Titanium were remelted by arc furnace in order to remove residual gases. Multicomponent alloy ingots with composition of (Cu_{0.5}Zr_{0.5})_{100-x}-(Ti_{x}Al_{1-x})_x (x = 0, 4, 6, 8, 9, 10, 12) were prepared by arc melting in a high purity argon atmosphere. Bulk cylindrical rods with a length of 50 mm and different diameters of 2–8 mm were prepared by copper mold casting in an argon atmosphere. Ribbon samples were prepared by melt spinning. The structures were examined by X-ray diffraction (XRD) with Cu Kα source. Optical microscopy (OM) was also used to examine the microstructure. The glass transition and the crystallization were examined by a differential scanning calorimeter (DSC) at a heating rate of 0.67 K/s. The melting points were measured by a differential thermal analysis (DTA) at a heating rate of 0.33 K/s.

3. Results

In order to evaluate the GFA of the (Cu_{0.5}Zr_{0.5})_{100-x}-(Ti_{x}Al_{1-x})_x alloys, we prepared the cylindrical rods with a diameter of 5 mm by copper mold casting. Figure 1 shows the XRD patterns of the as-cast rods with a diameter of 5 mm for each alloy. For the rods of Cu_{48}Zr_{48}Ti_{3}Al_{1} and Cu_{47}-Zr_{7}Ti_{13}Al_{1} alloys, the main phases are indexed as the glassy phase and ZrCu phase. For the Cu_{46}Zr_{44}Ti_{8}Al_{1} alloy, the main phases are identified as the ZrCu phase and AlTi phase.
The XRD patterns of the Cu46Zr45Ti4Al5 and Cu45Zr45Ti4Al5 alloys show broad diffraction maxima, which are the typical characteristic of the metallic glasses, indicating that these two alloys have high GFA. Furthermore, to examine the diameter dependence of GFA, we prepared the cylindrical rods with diameters of 5–7 mm for the Cu46Zr45Ti4Al5 and Cu45Zr45Ti4Al5 alloys. Figure 2 shows the XRD patterns of the bulk rods with diameters from 5 to 7 mm. To compare the results, we also indicate the XRD patterns of the melt-spun ribbons. It can be found that the XRD of the samples with diameters from 5 to 7 mm exhibit the same broad diffraction maxima as that of the ribbon sample for both alloys. For the 7-mm rod, the ZrCu phase appears. In addition, to sophisticate the GFA of these CuZrTiAl alloys, we prepared the as-cast rods of the Cu46Zr45Ti4Al5 alloy. Both samples exhibit the typical broad diffraction characteristic of metallic glass. Thus, the Cu45Zr45Ti4Al5 alloy exhibits higher GFA.

Figure 4 shows DSC curves of the melt-spun (Cu0.5Zr0.5)100–x(Ti0.5Al0.5)x, (x = 0, 4, 6, 8, 9, 10, 12) glassy alloys. Table 1 is the summary of the thermal results of the (Cu0.5Zr0.5)100–x(Ti0.5Al0.5)x glassy alloys. The glass transition, followed by a supercooled liquid region, and then exothermic reactions due to crystallization. The glassy alloys with x = 0, 4 and 6 exhibit a major sharp peak of crystallization. For the glassy alloys with x from 8 to 12, the crystallization process transforms to three exothermic events.

Table 1 Glass transition temperature \( T_g \), the onset temperature of crystallization, supercooled liquid region \( \Delta T_x = T_x - T_g \), liquidus temperature \( T_l \), reduced glass transition temperature \( T_r = T_g / T_l \) for the (Cu0.5Zr0.5)100–x(Ti0.5Al0.5)x, (x = 0, 4, 6, 8, 9, 10, 12) alloys, obtained by DSC and DTA using a heating rate of 40 and 20 K/min, respectively.

<table>
<thead>
<tr>
<th>( T_g ) (K)</th>
<th>( T_x ) (K)</th>
<th>( \Delta T_x ) (K)</th>
<th>( T_l ) (K)</th>
<th>( T_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = 0</td>
<td>682</td>
<td>727</td>
<td>46</td>
<td>1244</td>
</tr>
<tr>
<td>X = 4</td>
<td>686</td>
<td>744</td>
<td>59</td>
<td>1215</td>
</tr>
<tr>
<td>X = 6</td>
<td>688</td>
<td>754</td>
<td>66</td>
<td>1199</td>
</tr>
<tr>
<td>X = 8</td>
<td>691</td>
<td>741</td>
<td>50</td>
<td>1189</td>
</tr>
<tr>
<td>X = 10</td>
<td>693</td>
<td>732</td>
<td>39</td>
<td>1174</td>
</tr>
<tr>
<td>X = 12</td>
<td>698</td>
<td>737</td>
<td>39</td>
<td>1173</td>
</tr>
</tbody>
</table>
supercooled liquid region $\Delta T_s$, defined as $T_s - T_g$, is listed in Table 1 as well. The $T_s$ value increases slightly by adding Ti and Al elements, i.e., $T_s = 682$ K for the Cu$_{50}$Zr$_{50}$ alloy and $T_s = 698$ K for the Cu$_{50}$Zr$_{44}$Ti$_4$Al$_6$ alloy. On the other hand, the $T_g$ value increases up to $x = 6$ and then decreases with increasing Ti and Al contents to $x = 12$. As a result, there is a maximum value of $\Delta T_s = 66$ K for the Cu$_{50}$Zr$_{44}$Ti$_4$Al$_6$ alloy.

Figure 5 shows the DTA curves of the (Cu$_{6-x}$Zr$_{x}$)$_{100-x}$-(Ti$_{6}$Al$_{12}$)$_{x}$ alloys at a heating rate of 0.33 K/s. The arrows indicate the position of the liquidus temperature ($T_l$) (also listed in Table 1). The $T_l$ decreases evidently with increasing Ti and Al content. Furthermore, two endothermic melting peaks transform to only one peak with increasing the total content of Ti and Al from 0 to 12. One melting peak for the Cu$_{50}$Zr$_{44}$Ti$_4$Al$_6$ alloy indicates that this alloy lies very close to a quaternary eutectic point. Since the reduced glass transition temperature $T_g$ ($T_g$/$T_l$) has been confirmed to have strong correlation with GFA, $T_g$ is listed in Table 1 to evaluate the GFA of the (Cu$_{6-x}$Zr$_{x}$)$_{100-x}$-(Ti$_{6}$Al$_{12}$)$_x$ alloys. $T_g$ increases with the total content of Ti and Al increased. There is a tendency for $T_g$ to increase with increasing the GFA of the (Cu$_{6-x}$Zr$_{x}$)$_{100-x}$-(Ti$_{6}$Al$_{12}$)$_x$ alloys. However, the Cu$_{50}$Zr$_{44}$Ti$_4$Al$_6$ alloy is the exception to the observed trends in $T_g$ and GFA.

4. Discussion

It is well known that the alloys with high GFA usually satisfy the following three factors, i.e., (1) multi-component system consisting of more than three elements, (2) significant atomic size mismatches about above 12% among the three main elements, and (3) negative heats of mixing among their elements. For the Cu-Zr-Ti-Al system, the negative mixing enthalpy is $-23$ kJ/mol for Cu-Zr, $-9$ kJ/mol for Cu-Ti, $-1$ kJ/mol for Cu-Al, $-44$ kJ/mol for Zr-Al, $-30$ kJ/mol for Ti-Al, 0 kJ/mol for Zr-Ti. The atomic radii of Cu is 0.128 nm, 0.16 nm for Zr, 0.143 nm for Al, and 0.145 nm for Ti. The ratios of the atomic radius (R) are 1.25 for Zr/Cu, 1.13 for Ti/Cu, 1.11 for Al/Cu, 1.12 for Zr/Al, and 1.01 for Ti/Al. It can be recognized that the CuZrTiAl alloy system satisfies these three component rules. It has previously been reported that large atomic size ratios and negative heat of mixing can produce an efficiently dense random packing structure in the liquid, which can reduce long-range rearrangement of all the elements. The present results also demonstrate that the alloy with good GFA in the (Cu$_{6-x}$Zr$_{x}$)$_{100-x}$-(Ti$_{6}$Al$_{12}$)$_x$ alloys lies near a quaternary eutectic point. It is obvious that the simultaneous addition of Ti and Al is very efficient in improving the stabilization of the supercooled liquid, which hinders the nucleation and growth of the crystalline phases and thus improves the GFA. Consequently, the simultaneous addition of Ti and Al leads to high GFA of quaternary CuZrTiAl alloys.

Although the Cu$_{50}$Zr$_{44}$Ti$_4$Al$_6$ alloy is located at a quaternary eutectic point, this alloy exhibits rather low GFA (as shown in Fig. 1). The displacement of best glass-forming compositions from eutectic compositions may be attributable to asymmetry in the coupled zone. Figure 6 shows the optical micrograph of the central part of the cross-section of 5 mm as-cast rod. It is seen that the microstructure consists of the eutectic phase together with the primary TiAl phase, which is indicated by black arrows. This clearly demonstrates that the final structure of the Cu$_{44}$Zr$_{44}$Ti$_6$Al$_6$ quaternary eutectic alloy changes to a primary phase in eutectic matrix, not a single eutectic phase. The precipitation of the competing TiAl phase would significantly hinder the formation of the glassy phase, which leads to low GFA of the Cu$_{44}$Zr$_{44}$Ti$_6$Al$_6$ alloy.

5. Conclusion

The simultaneous addition of Ti and Al is effective for an increase in GFA of the binary Cu$_{50}$Zr$_{50}$ alloy. As the content of Ti and Al increases from 0 to 10 at%, the GFA of the quaternary Cu-Zr-based alloys increases. The critical diameter of the Cu$_{50}$Zr$_{50}$Ti$_4$Al$_4$ and Cu$_{50}$Zr$_{50}$Ti$_4$Al$_6$ alloys is up to 6 mm. Moreover, we found that the critical diameter of a glassy rod is 7 mm for the Cu$_{44.5}$Zr$_{44.5}$Ti$_{4.5}$Al$_{5.5}$ alloy. The compositions of these alloys with high GFA are closer to a
CuZrTiAl quaternary eutectic. Although the \(\text{Cu}_{44}\text{Zr}_{44}\text{Ti}_{6}\text{Al}_{6}\) alloy locates at a quaternary eutectic point, this alloy exhibits rather low GFA. Much higher contents of Ti and Al lead to the precipitation of the simple TiAl phase, which degrades the GFA of the alloys.

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