Complete Composition Tunability of Cu(Ni)-Ti-Zr Alloys for Bulk Metallic Glass Formation

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In the Cu-Zr-Ti ternary system, a new composition zone of bulk metallic glasses (BMGs) formation was discovered, locating at the 55–57 at. pct Cu, 30–31 at. pct Ti and 13–14 at. pct Zr, and near Cu-Ti binary subsystem rather than the Cu-Zr binary. For these alloys, BMG rods of 2 mm in diameter can be fabricated by using copper mold casting. It is expected that these BMG-forming alloys correlate with ($L\rightarrow CuTi+Cu_2TiZr+Cu_3Zr_1$) eutectic reaction that the undercooled melt undergoes during solidification. Adopting “3D pinpointing approach”, compositional dependence of glass-forming ability (GFA) in Cu(Ni)-Ti-Zr pseudo ternary system was revisited. Optimized BMG-forming composition is located at Cu$_{50.4}$Ni$_{5.6}$Ti$_{33.1}$Zr$_{13}$, with a critical diameter of 6 mm for complete BMG formation. Its GFA is significantly superior to Vit 101 (Cu$_{47}$Ni$_{5.8}$Ti$_{34}$Zr$_{11}$) previously developed by Caltech group. The effect that the GFA of the ternary base alloy was improved by substitution of Ni for Cu is attributed to a role of retarding the crystallization of Cu.

KEY WORDS: Bulk metallic glasses; Amorphous alloys; Eutectic; Copper

1. Introduction

Over the past decade, a large number of new bulk metallic glass-forming alloys have been discovered[1,2]. Among these newly-developed bulk metallic glasses (BMGs), the Cu-based BMGs are particularly of interest as potential engineering materials due to their advantages in several aspects such as relatively low cost, high fracture strength ($\sim$2 GPa) coupled with accessible compressive malleability[3,4], high fracture toughness[5] and relatively easy glass formation. Since the first Cu-based BMG former Cu$_{47}$Ni$_{5.8}$Ti$_{34}$Zr$_{11}$ (Vit 101) was discovered in 1995[6], critical size ($D_c$) of BMG formation had been upgraded up to centimeter scale, based on the Cu-Zr or Cu-Hf alloys such as Cu$_{46}$Zr$_{13}$Al$_2$V$_5$[7], Cu$_{46.25}$Zr$_{42.25}$Al$_{7.5}$Er$_2$[8], Cu$_{46}$Zr$_{12}$Al$_2$Be$_7$[9], Cu$_{44.25}$Ag$_{54.75}$Zr$_{36}$Ti$_{10}$[10], Cu$_{46}$Hf$_{32}$Al$_9$[11] and a new Cu$_{45}$Zr$_{22.5}$Y$_{3.45}$Al$_9$[12] (with a maximum $D_c$ of 14 mm under copper mold casting). However, improvement of the glass-forming ability (GFA) for Cu-Ti based alloy remains limited via further multi-component alloying approach[13–16].

Further more, it was revealed that even in a given ternary system, it is feasible that multiple composition zones with a capability for BMG formation are present, which correlate with their respective “deep eutectic” reactions[17]. Recently, it is demonstrated that in the Cu-Zr-Ti ternary system, there exist two BMG-forming composition zones in proximity of Cu$_{46}$Zr$_{13}$Ti$_7$ and Cu$_{52}$Zr$_{40}$Ti$_8$, respectively, which are near Cu-Zr subsystem and correlate with the $[L\rightarrow Cu_3Zr(Ti)_7]+Cu_{10}Zr(Ti)_7$ and $[L\rightarrow Cu_{10}Zr(Ti)_7]+Cu_3Zr(Ti)_7$ invariant eutectic reaction, respectively[18,19]. As a consequence, it is of interest whether additional BMG-forming composition zone is present near Cu-Ti subsystem in the Cu-Zr-Ti ternary.

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Fig. 1 Partial phase diagram of liquidus projection at Cu-rich corner for Cu-Ti-Zr ternary system from literature[20]. The tie-lines between the compounds are drawn, showing different phase boundaries. A small triangle with equal sides represents the investigated composition region. Within it, optimal BMG-forming composition zone is marked by a circled area

Currently, phase diagram of liquidus projection of the Cu-Ti-Zr ternary system has not been well established[20–23]. Figure 1 displays a portion near the Cu-Ti side in the diagram given by Woychik and Massalski[20]. In this region, it was given that there is a ternary eutectic reaction of ($L\rightarrow CuTi+Cu_2Ti+Cu_3TiZr$) with an invariant temperature of about 1123 K. An additional contribution was made from the CALPHAD results[21], for which a eutectic reaction of ($L\rightarrow CuTi+Cu_2Ti+Cu_3TiZr$)
with an invariant temperature of 1128 K was predicted. These two probably involved reactions and phase boundaries are drawn as the triangles in Fig. 1. Nevertheless, such low temperatures at which the liquid remains stable, more or less, provide a clue of easy glass formation within this composition region.

The purpose of this paper is threefold. First, compositional dependence of the GFA in the Cu-Ti-Zr ternary system near the Cu-Ti subsystem was revisited, starting from Cu_{55}Ti_{35}Zr_{10} that was reported to have the $D_c$ of $\sim$0.5 mm [6]. We will demonstrate a new composition region within which the 2 mm-diameter BMGs can be fabricated. Second, Ni was selected to substitute for Cu, and the optimal BMG-forming alloy was located in the Cu-Ni-Ti-Zr quaternary system using the “3D pinpointing approach” [24, 26], by virtue of which a number of new BMGs with record size have been discovered in several quaternary systems including the Mg- [24, 26], Cu- [10, 12] and Hf-based [27]. The third aspect is a characterization of the microstructure of arc-melted alloys with optimal BMG-forming composition in the ternary and quaternary. The detailed information regarding phase selection and morphology is used to establish the correlation between the BMG-forming composition and the eutectic reaction that the liquid undergoes during cooling with and without Ni substitution.

2. Experimental

Elemental pieces with purity better than 99.9% were used as starting materials. The master alloy ingots of 20 g in weight with the nominal composition (in atomic percentage) were prepared by arc melting under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The alloy ingots were melted several times to ensure compositional homogeneity. The weight change of the master alloys before and after arc-melting is less than 0.1 wt pct. For smaller samples (diameter $\leq$3 mm), the master alloy was re-melted and sunk into the copper mold in a mini arc-melter. To produce rods with a diameter larger than 4 mm, the master alloy re-melted in a tilting mold. To produce rods with a diameter larger than 4 mm, the master alloy re-melted in a tilting mold. To produce rods with a diameter larger than 4 mm, the master alloy re-melted in a tilting mold. To produce rods with a diameter larger than 4 mm, the master alloy re-melted in a tilting mold.

The as-cast rods and arc-melted ingots were sectioned transversely and polished for X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) observation. XRD analysis of the samples was carried out in a Rigaku D/ max 2400 diffractometer with monochromated CuK$\alpha$ radiation ($\lambda=0.1542$ nm). SEM observation was performed in a Quanta 600 scanning electron microscope. Samples for transmission electron microscopy (TEM) observations in FEI Tecnai F30 were prepared by twin-jet electropolishing, with a solution of 9 vol. pct nitric acid in a mixture of methanol and butoxyethanol (2:1).

The glass transition and crystallization behavior of the as-cast glassy rods were investigated in a Perkin-Elmer differential scanning calorimeter (DSC-diamond) with alumina container under flowing purified argon at a heating rate of 0.67 K s$^{-1}$. A second run under identical conditions was used to determine the baseline after each run. To confirm the reproducibility of the experimental results, at least three samples have been measured for each composition. All the measurements of the glass transition temperature ($T_g$) and onset temperature of crystallization events ($T_{c1}$) were reproducible within the error of $\pm 1$ K. The melting behavior of the alloys was measured in a Netzsch 404 DSC with alumina container, using the heating and cooling rates of 0.33 K s$^{-1}$.

3. Results

3.1 Compositional dependence of BMG formation around Cu$_{55}$Ti$_{35}$Zr$_{10}$ alloy

Figure 2 shows a composition map of BMG formation for the 2 mm-diameter as-cast rods. The investigated composition region is within a compositional triangle of 50–70 at. pct Cu, 25–45 at. pct Ti, 5–25 at. pct Zr. Its location in the phase diagram is drawn as an equal-sides triangle in Fig. 1. In Fig. 2, the open, half open and full circle symbols represent the formation of crystalline, partially glassy phase and complete glassy phase, respectively, at the composition. Starting alloy, Cu$_{55}$Ti$_{35}$Zr$_{10}$, is marked by an arrow for comparison.
The exothermic crystallization peaks are observed in each alloy. Based on the Eq. (2) and related data in literature [21], cooling rate of arc-melted Cu-Ti-Zr ingot can be estimated to be in a range of ~2–15 K·s⁻¹. At such cooling rate, solidified microstructure in the center of the ingot can be directly associated with the phase selection when the alloy melt crystallizes before freezing into a glass, i.e., its non-equilibrium solidification pathway prior to glass formation.

Figure 4(a) illustrates the XRD patterns taken from the cross-sectional surface of the 3 mm-diameter as-cast rod and arc-melted ingot for Cu₅₆Ti₃₁Zr₁₃ ternary alloy. In both cases, the identified crystalline phases are completely identical. Three intermetallic phases, γ-CuTi (tetragonal, a=0.3118 nm, c=0.5887 nm, space group P4/mnm), Cu₅₁Zr₁₄ (hexagonal, a=1.1235 nm, c=0.8271 nm, space group P6/m) and Cu₂TiZr (MgZn₂-type Laves phase, a=0.51491 nm, c=0.84211 nm, space group P63/mmc) are included, as seen in Fig. 4(a).

Table 1

<table>
<thead>
<tr>
<th>Alloys (at. pct)</th>
<th>CuₓNi₁₋ₓ</th>
<th>Dmax/mm</th>
<th>Tg/K</th>
<th>Tm/K</th>
<th>∆Tg/K</th>
<th>Tl/K</th>
<th>Tg/K</th>
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<tr>
<td>Cu₅₀Ti₃₁Zr₁₃</td>
<td>x=0</td>
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<td>684</td>
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<td>1106</td>
<td>1164</td>
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<td>700</td>
<td>726</td>
<td>26</td>
<td>1101</td>
<td>1141</td>
</tr>
<tr>
<td>Cu₅₀₅₄Ni₅₆₅₁Zr₃₁</td>
<td>x=0.1</td>
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<td>695</td>
<td>724</td>
<td>29</td>
<td>1104</td>
<td>1138</td>
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<tr>
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<td>691</td>
<td>713</td>
<td>21</td>
<td>1105</td>
<td>1163</td>
</tr>
<tr>
<td>Cu₃₇₂₇₃₁₇₃₁₃</td>
<td>x=0.15</td>
<td>3</td>
<td>671</td>
<td>717</td>
<td>46</td>
<td>1105</td>
<td>1160</td>
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</table>

(∆Tg, ∆Tc=Tc1–Tg) around 36 K. Figure 3(c) shows a DSC curve during the heating and cooling runs near the melting temperature for Cu₅₆Ti₃₁Zr₁₃ alloy as the representative. It is observed in the curve that three main events take place during either melting or solidifying procedure, implying that the alloy is off-eutectic. The onset and end temperature of the melting event is marked with arrows and labeled as Tm and Tl on the curve, respectively. The Tl is determined to be around 1106 K. It is about ~20 K lower than the eutectic temperatures of both (L→Cu₅₁Ti₃₁Zr₁₃)+(Cu₂TiZr)²⁰ and (L→Cu₅₁Ti₃₁Zr₁₃)+(Cu₂TiZr)²¹. It implies that the alloys in proximity of Cu₅₆Ti₃₁Zr₁₃ probably do not relate to these two reactions, and their liquid is more stable. With the Tl value of 1164 K, the reduced glass transition temperature (Tg/Tl, Tg=Tg/Tl) of Cu₅₆Ti₃₁Zr₁₃ alloy was calculated to be 0.59. Thermal properties, including Tg, Tc₁, ∆Tc, Tm, Tl and Tg for the Cu₅₆Ti₃₁Zr₁₃ alloy as the typical are listed in Table 1.

3.2 Phase selection of arc-melted Cu₅₆Ti₃₁Zr₁₃ BMG-forming alloy

To reveal the crystalline phases competing with glass formation and the eutectic reaction that the liquid of BMG-forming alloy undergoes during solidification, phase selection of the 3 mm-diameter as-cast rods (slightly larger than Dc) and arc-melted ingot of Cu₅₆Ti₃₁Zr₁₃ alloy (Dc=2 mm) were identified. Based on the Eq. (2) and related data in literature [28], cooling rate of arc-melted Cu-Ti-Zr ingot can be estimated to be in a range of ~2–15 K·s⁻¹. At such cooling rate, solidified microstructure in the center of the ingot can be directly associated with the phase selection when the alloy melt crystallizes before freezing into a glass, i.e., its non-equilibrium solidification pathway prior to glass formation.
Table 2 Chemical compositions of different phases in arc-melted typical Cu(Ni)-Ti-Zr BMG-forming alloys, determined by EDX analysis. Experimental error of measurements is estimated to be ±1 at. pct.

<table>
<thead>
<tr>
<th>Alloys/at. pct</th>
<th>Area</th>
<th>Cu/at. pct</th>
<th>Ti/at. pct</th>
<th>Zr/at. pct</th>
<th>Ni/at. pct</th>
<th>Normalized phase</th>
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<tr>
<td>Cu_{56}Ti_{31}Zr_{13}</td>
<td>A</td>
<td>49</td>
<td>48.5</td>
<td>2.5</td>
<td>–</td>
<td>γ-CuTi</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>51</td>
<td>28</td>
<td>21</td>
<td>–</td>
<td>Cu₂TiZr</td>
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<td>C</td>
<td>75</td>
<td>4.5</td>
<td>20.5</td>
<td>–</td>
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<tr>
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<td>49</td>
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<td>1.5</td>
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<td>B</td>
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<td>28.5</td>
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<td>4</td>
<td>Cu₂TiZr</td>
</tr>
<tr>
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<td>C</td>
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<td>2.5</td>
<td>22.5</td>
<td>1.5</td>
<td>Cu₅₁Zr₁₄</td>
</tr>
<tr>
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<td>48</td>
<td>48.5</td>
<td>2</td>
<td>1.5</td>
<td>γ-CuTi</td>
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<tr>
<td></td>
<td>B</td>
<td>50</td>
<td>25</td>
<td>18</td>
<td>7</td>
<td>Cu₂TiZr</td>
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<tr>
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<td>48</td>
<td>48</td>
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<tr>
<td></td>
<td>B</td>
<td>48</td>
<td>22</td>
<td>21</td>
<td>9</td>
<td>Cu₂TiZr</td>
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</table>

Fig. 4 (a) XRD patterns taken from the cross-sectional surface of the arc-melted ingot and 3 mm-diameter as-cast rod for the Cu_{56}Ti_{31}Zr_{13} alloy, and (b) Backscattered SEM image of the Cu_{56}Ti_{31}Zr_{13} arc-melted ingot.

The region of A (darker and acicular), B (gray and dendrite-like) and C (lighter) can be identified as γ-CuTi, Cu₂TiZr and Cu₅₁Zr₁₄, respectively. It is consistent with the results from XRD analysis, as shown in Fig. 4(a). In addition, it is indicated that the Zr of ~2 at. pct and Ti of ~4 at. pct are dissolved in the γ-CuTi and Cu₅₁Zr₁₄ binary compounds, respectively. Furthermore, as seen in Fig. 4(b), the coarse and acicular γ-CuTi phase seems to be a primary phase during solidification. Small fraction of couple-grown (γ-CuTi+Cu₅₁Zr₁₄) colony (eutectic feature) can be observed, as marked as circles in Fig. 4(b). In the matrix with a large fraction of Cu₂TiZr, co-existence of three phases, γ-CuTi, Cu₅₁Zr₁₄ and Cu₂TiZr, is presented.

3.3 Optimizing BMG-forming composition in Cu-Ni-Ti-Zr quaternary system using the “3D pinpointing approach”

As shown by Caltech group[6], the GFA of Cu-Ti-Zr ternary alloy can be enhanced by substitution of Ni for Cu. However, the full potential of BMG formation in Cu(Ni)-Ti-Zr quaternary alloys has not been uncovered without systematic investigation. In light of the similarity in chemistry and atomic size between Cu (r_{Cu}=0.128 nm) and Ni (r_{Ni}=0.127 nm), the Cu-Ni-Ti-Zr quaternary can be treated as the (Cu, Ni)-Ti-Zr pseudo ternary. Then, the “3D pinpointing approach” is adopted to locate the optimal BMG-forming composition as follow. Compositional dependence of the GFA on several consecutive compositional planes were examined, each with a fixed Ni to Cu ratio expressed as Cu_{1-x}Ni_{x} (x=0.05, 0.1 and 0.15, respectively).

Figures 5(a)–(c) display the composition maps of BMG formation for 4 mm-diameter as-cast rods on the three composition planes. On the x=0.05 plane, a composition with a Dc of 4 mm is obtained at Cu_{53.2}Ni_{2.8}Ti_{30}Zr_{14}, as seen in Fig. 5(a). With respect to the Cu_{56}Ti_{31}Zr_{13} (Dc=2 mm), the Dc was doubled immediately, indicating that minor Ni substitution for Cu has a significant effect to elevate the GFA. When the Ni to Cu ratio increased up to x=0.1, the best glass former is located at Cu_{50.4}Ni_{5.6}Ti_{31}Zr_{13}, resulting in the Dc reaching 6 mm. On further increasing the Ni to Cu ratio up to x=0.15, the GFA is degraded conversely. On this plane, the Dc of all investigated alloys is smaller than 4 mm. In addition, it is worthy to highlight that...
Fig. 5 Composition maps of BMG formation for 4 mm-diameter rods at several (Cu, Ni)-Ti-Zr compositional planes with the ratios of Cu$_{1-x}$Ni$_x$: (a) $x=0.05$, (b) $x=0.1$ and (c) $x=0.15$. Cu$_{47}$Ni$_8$Ti$_{34}$Zr$_{11}$ alloy (Vit 101) was marked by an arrow for comparison in (c).

the Vit 101 can be reduced as the (Cu$_{0.85}$Ni$_{0.15}$)$_{55}$Ti$_{34}$Zr$_{11}$ and is marked as an arrow in Fig. 5(c). Under our experimental condition, the $D_c$ of Vit 101 was determined to be 3 mm only. Evidently, the GFA of Cu$_{50.4}$Ni$_{5.6}$Ti$_{30}$Zr$_{14}$ ($D_c=6$ mm) we optimized in this system is significantly stronger than that of Vit 101.

Figures 6(a) and (b) display the XRD patterns and DSC scans of as-cast rods with maximum $D_c$ ($D_{\text{max}}$) on each compositional plane, Cu$_{53.3}$Ni$_{2.9}$Ti$_{30}$Zr$_{14}$, Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$ and Cu$_{49.75}$Ni$_{8.25}$Ti$_{33}$Zr$_{13}$. Besides diffusive maxima from the amorphous phase, no any diffraction peak from crystalline phases is detectable, indicating the complete glass formation in all cases.

As shown in Fig. 6(b), the crystallization of Ni-containing quaternary BMGs proceeds through three steps, and the heat release caused by first event become larger with increasing the Ni content in the alloys, compared with the Ni-free ternary (see Fig. 3(b)).

Figure 6(c) shows DSC curves during the heating and cooling runs for three representative alloys, near and above their melting temperatures. Different from the ternary base alloy (see Fig. 3(c)), only two endothermic events appear in the curves for these
quaternary alloys. Thermal properties obtained from DSC measurements, including $T_g$, $T_m$, $\Delta T_x$, $T_m$, $T_L$, and calculated $T_g$ values, for three typical quaternary BMGs are also tabulated in Table 1. It is noticed that the $\Delta T_x$ value of all Ni-containing quaternary BMGs is somewhat smaller than that of the Cu$_{50}$Ti$_{31}$Zr$_{13}$ ternary alloy. It demonstrates that the GFA is not necessarily correlated with the magnitude of $\Delta T_x$. Compared with the Cu$_{50}$Ti$_{31}$Zr$_{13}$ ternary alloy, the $T_m$ of Ni-containing quaternary alloys remains unchanged within experimental error, but the optimal quaternary alloy, Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$, has the lowest $T_L$ value (1138 K) among all alloys, which is $\sim$26 K lower than that of the ternary Cu$_{50}$Ti$_{31}$Zr$_{13}$. Evidently, partial substitution of Ni for Cu in the Cu-Ti-Zr base alloy has an appreciable effect of depressing the liquidus. Additionally, the $T_g$ value of the Cu$_{53.2}$Ni$_{12.8}$Ti$_{30}$Zr$_{14}$ and Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$ BMGs reaches up to 0.61. It is consistent with the fact that their GFA is higher than that of the Cu$_{50}$Ti$_{31}$Zr$_{13}$ and Cu$_{46.75}$Ni$_{25}$Ti$_{33}$Zr$_{12}$ (see Table 1).

Figures 7(a) and (b) display the TEM bright-field image and corresponding selected area electron diffraction (SAED) pattern, respectively, for a 6 mm-diameter as-cast rod of the optimized Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$ alloy. The sample was taken from the center of the as-cast rod. The uniform and contrastless feature in the image and a broad halo in the SAED pattern indicate the formation of a single amorphous phase in the rod. Furthermore, as shown in Fig. 7(c), the high-resolution TEM image also confirms that there is no distinguishable crystallite even on nano-scale corroborating the XRD result that the material is fully amorphous. These findings support our claim regarding the D$_c$ of the optimized Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$ alloy, excluding the arguments such as that the D$_c$ of Cu$_{47}$Ni$_{38}$Ti$_{14}$Zr$_{11}$ and Cu$_{47}$Ni$_{38}$Ti$_{33}$Zr$_{11}$Si$_{1}$ was over-evaluated since the nanocrystals are unavoidable in the samples.$^{[25,30]}$

3.4 Phase selection of arc-melted Cu(Ni)-Ti-Zr quaternary alloys

To address the role that the Ni substitution plays for elevating the GFA of Cu-Ti-Zr alloys, phase selection of several arc-melted Cu(Ni)-Ti-Zr BMG-forming alloys with different ratios of the Ni to Cu is investigated.

Figure 8 shows the XRD patterns taken from the cross-sectional surfaces of the arc-melted ingots for the optimized glass former on each compositional plane ($x=0.05$, 0.1, 0.15, respectively). Similar to the Cu$_{56}$Ti$_{33}$Zr$_{11}$ ternary (see Fig. 4(b)), three intermetallic compounds, γ-CuTi, Cu$_2$TiZr and Cu$_3$Zr$_{14}$, are identified from the patterns. It indicates that until Ni substitution at $x=0.15$, no new crystalline phase competing with glass formation is involved. Nevertheless, it is found that the diffraction peaks of Cu$_{53}$Zr$_{14}$ phase fade away as the Ni content increased, as seen in Fig. 8. This suggests that partial substitution of Ni for Cu has an effect of retarding the formation of Cu$_{53}$Zr$_{14}$ binary compound.

Figure 9(a), (c) and (e) show BSEM images taken from the cross-sectional surface of arc-melted ingots for the Cu$_{53.2}$Ni$_{12.8}$Ti$_{30}$Zr$_{14}$ ($x=0.05$), Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$ ($x=0.1$) and Cu$_{46.75}$Ni$_{25}$Ti$_{33}$Zr$_{12}$ ($x=0.15$), respectively. Figure 9(b), (d) and (f) are higher magnification images for the boxed areas in Fig. 9(a), (c) and (e), respectively. Chemical compositions of the phases with different contrast are determined by EDX analysis from the average of at least five measurements, and listed in Table 2. As shown in Fig. 9(a), morphology of solidified microstructure for the alloy of 2.8 at. pct
Ni substitution is similar to that of the Cu$_{56}$Ti$_{31}$Zr$_{13}$ ternary (see Fig. 4(b)), but the microstructure is obviously refined in contrast to the ternary. It can be seen that the $\gamma$-CuTi primary phase (A) in acicular shape disperses in the three phases co-existing matrix, namely, the eutectic colony consisting of the $\gamma$-CuTi, Cu$_{51}$Zr$_{14}$ (C) and Cu$_2$TiZr (B). Clearly, Ni addition even with a small amount suppresses the solute partition in the melt during solidification. EDX analysis indicates that the solubility of Ni in Cu$_2$TiZr is much larger than that in $\gamma$-CuTi or Cu$_{51}$Zr$_{14}$, as seen in Table 2. Increasing the ratio up to $x=0.1$, the microstructure for Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$ significantly changed. As shown in Fig. 9(c) and (d), the $\gamma$-CuTi phase (A) remains solidified as primary phase but in spherical shape no longer in the needle-like form. In the remaining matrix, fine acicular rods of $\gamma$-CuTi are surrounded by Cu$_2$TiZr phase (B). Such a microstructure is typical of the morphology observed for non-faceted–faceted eutectics (like Al-Si or Fe-C binary)\textsuperscript{[31]}, indicative of the presence of pseudo binary eutectic coupled with the $\gamma$-CuTi and Cu$_2$TiZr. Due to the small fraction, if any, Cu$_{51}$Zr$_{14}$ phase is invisible even if it is detectable in the XRD pattern (see Fig. 8). For the Cu$_{46.75}$Ni$_{8.25}$Ti$_{33}$Zr$_{12}$ alloy at $x=0.15$, the microstructure exhibits a typical eutectic morphology of the $\gamma$-CuTi (A) and Cu$_2$TiZr (B) co-existing, with a couple-growth lamella feature, as

Fig. 9 Backscattered SEM images of the arc-melted ingots for three (Cu, Ni)-Ti-Zr quaternary alloys with the maximum $D_c$ at each compositional plane respectively: (a) Cu$_{53.2}$Ni$_{2.8}$Ti$_{30}$Zr$_{14}$, (c) Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$ and (e) Cu$_{46.75}$Ni$_{8.25}$Ti$_{33}$Zr$_{12}$; (b), (d) and (f) are the high magnification view of the selected area in (a), (c) and (e), respectively.
seen in Fig. 9(f). Similarly, the Cu$_5$Zr$_{14}$ phase is not observed in this alloy either. Moreover, in the two cases, the Ni mainly dissolves in the Cu$_2$TiZr ternary compound, as shown in Table 2. We noticed that the Cu$_{51}$Zr$_{14}$ phase remains present in the Cu$_2$Ni$_6$Ti$_{33}$Zr$_{11}$ rapidly-solidified powders annealed at 1073 K$^{[22]}$. It demonstrates that the Cu$_{51}$Zr$_{14}$ phase in the Cu(Ni)-Ti-Zr alloys is easy to be suppressed during deep undercooling.

4. Discussion

As shown in our previous work, two BMG-forming composition zones around the Cu$_{56}$Zr$_{30}$Ti$_{7}$[18] and Cu$_{52}$Zr$_{40}$Ti$_{10}$[19] has been uncovered in the Cu-Zr-Ti system near Cu-Zr subsystem. These two zones are along, although slightly off, the invariant eutectic groove for the reaction of ($L$→Cu$_9$Zr$_3$+Cu$_{11}$Zr$_7$) and ($L$→Cu$_{10}$Zr$_5$+Cu$_3$Zr), respectively. Adding the current finding around the Cu$_{56}$Ti$_{33}$Zr$_{13}$, at least three composition zones for BMG formation have been settled in this ternary system. Each zone correlates with their respective eutectic reaction. However, the GFA of the Cu-Ti based alloy (e.g. $D_c=2$ mm for Cu$_{56}$Ti$_{33}$Zr$_{13}$) is weaker than that of the Cu-Zr based one ($D_c=4$ mm for both of the Cu$_{50}$Zr$_{29}$Ti$_{21}$[18] and Cu$_{52}$Zr$_{40}$Ti$_{10}$[19]). It can be understood from the chemical interaction between the constituents. With respect to the Cu-Zr pairs, the interaction between Cu and Ti is somewhat weak, as indicated by the more negative heat of mixing for Cu-Zr ($\Delta H_{\text{mix}}=-23$ kJ/mol) than that for Cu-Ti ($\Delta H_{\text{mix}}=9$ kJ/mol)$^{[33]}$. The stronger interaction between unlike atoms in the liquid results in a denser packing of the atoms. It makes the liquid more stable, then favoring the glass formation.

As shown in the current work, partial substitution of Ni for Cu in the Cu-Ti based alloys has a significant effect to enhance the glass formation. Meanwhile, such a substitution if the concentration less than 8 at. pct does not create new crystalline phase competing with glass formation with respect to the base ternary alloy. It implies that the Ni addition plays a role to frustrate the formation of intermetallics such as Cu$_{51}$Zr$_{14}$ to make the solute partition difficult in the liquid during undercooling. Regarding the minor difference in atomic size between Cu and Ni, topological effect on the GFA seems no longer as the dominant issue$^{[34–36]}$. As a matter of fact, the Cu-Ni-Ti-Zr quaternary alloys can be treated as a “topologically pseudo ternary system”. On the other hand, with respect to the Cu-Ti and Cu-Zr pairs, the chemical interaction of Ni with the Ti and Zr is much stronger, as indicated by the more negative $\Delta H_{\text{mix}}$ for the Ni-Ti ($\Delta H_{\text{mix}}=-35$ kJ/mol) and Ni-Zr ($\Delta H_{\text{mix}}=-49$ kJ/mol) than that for Cu-Ti and Cu-Zr$^{[33]}$, where as the affinity of Cu-Ni pairs is negligible ($\Delta H_{\text{mix}}=4$ kJ/mol). Consequently, as substitutional solutes for Cu, the Ni addition at an appropriate concentration would enhance the local chemical short-range order and help to improve the atomic pack efficiency of the liquid, then restrain atomic mobility, as manifested by lowering the liquidus temperature by as much as about 26 K compared with the Cu-Ti-Zr ternary subsystem.

5. Conclusions

(1) In the Cu-Zr-Ti ternary system, a new composition zone with a capability to form bulk metallic glasses was discovered, located at the 55–57 at. pct Cu, 30–31 at. pct Ti and 13–14 at. pct Zr, and near Cu-Ti binary subsystem. Within this composition region, BMG rods of 2 mm in diameter can be fabricated by using copper mould casting. Such easy glass-forming feature is expected to correlate with ($L$→Cu$_{10}$Ti$_5$+Cu$_{2}$Zr$_{14}$+Cu$_{51}$Zr$_{14}$) eutectic reaction. Combined with the previous work$^{[18,19]}$, it is revealed that there exist at least three BMG-forming composition zones in the Cu-Zr-Ti ternary system, related to their respective deep eutectic reactions in the phase diagram.

(2) Undergoing a systematic investigation with “3D pinpointing approach”, the optimized BMG-forming composition in the Cu(Ni)-Ti-Zr pseudo ternary system is located at Cu$_{50.4}$Ni$_{5.6}$Ti$_{31}$Zr$_{13}$. The critical diameter of BMG formation is elevated up to 6 mm. The glass-forming ability of this composition is significantly superior to Vit 101 (Cu$_{47}$Ni$_{34}$Zr$_{19}$) previously developed by Caltech group. The effect that the GFA of the ternary base alloy was improved by substitution of Ni for Cu is attributed to retarding the crystallization of Cu$_{51}$Zr$_{14}$ intermetallics.

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