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Abstract: The formation of bulk metallic glasses (BMGs) in ternary Cu-Zr-Ti system was investigated by a copper mold casting method. The nature of the amorphous phase was verified by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). It was demonstrated that the BMGs could be formed in a broad composition range in this system. $Cu_{50}Zr_{42.5}Ti_{7.5}$, $Cu_{60}Zr_{27.5}Ti_{12.5}$, $Cu_{60}Zr_{30}Ti_{10}$ and $Cu_{60}Zr_{32.5}Ti_{7.5}$ alloys exhibit strong glass-forming ability (GFA), and fully glassy rods of 5 mm in diameter can be obtained. In the center region of the ternary diagram, however, the GFA of the alloys was degraded due to the presence of Laves phase. The degradation of the GFA results from easy nucleation of the Laves phase in the undercooled liquid.

Key words: bulk metallic glass; glass-forming ability; Laves phase; eutectics

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1. Introduction

The alloys with a composition close to deep eutectics have a more stable undercooled liquid and slower kinetics of crystallization upon cooling than the off-eutectic compositions, and often show better glass forming ability (GFA) [1], such as $Mg_{65}Cu_{25}Y_{10}$ [2-3], $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ [4], $Pt_{60}Cu_{20}P_{20}$ [5], $Cu_{46}Zr_{42}Al_7Y_5$ [6], $(Fe_{44.3}Cr_5Co_5Mo_{12.8}Mn_{11.2}C_{15.8}B_{5.9})_{98.5}Y_{1.5}$ [7] and so on. Therefore, generally it is necessary to locate the eutectics in multicomponent systems for the search of bulk metallic glass (BMG) forming alloys. Cu-Zr-Ti system exhibits multiple deep eutectics, and one expects that this ternary system can own good glass-forming ability. It has been reported that $Cu_{60}Zr_{30}Ti_{10}$ exhibits best GFA in $Cu_{60}Zr_{40-x}Ti_x$ alloys and the BMG of 4 mm in diameter can be produced [8-9]. Thus, it is a good opportunity to investigate the effect of deep eutectics on GFA because normally it is a difficult job to find the eutectics in multicomponent systems. In this paper, the bulk glass formation in the Cu-Zr-Ti system was investigated in detail, and it is found that the BMGs up to 5 mm in diameter can be formed in a broad composition range. The glass formation, thermal stability and the effect of deep eutectics on GFA in the Cu-Zr-Ti system were also reported.

2. Experimental procedure

The alloy ingots were prepared by arc melting the mixtures of pure Cu, Zr and Ti in a purified argon atmosphere. The cylindrical rods with diameters from 1 to 6 mm were prepared by a copper mould casting method. In addition, the ribbon samples with a cross section of 0.02 mm×2 mm were prepared by the melt spinning technique. The glassy structure was examined by X-ray diffraction (XRD). The thermal stability and melting behavior were examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s.

3. Results

The critical diameters for glass formation of ternary Cu-Zr-Ti alloys are shown in Fig. 1. It can be observed that the glass-forming ability was improved in the ternary system firstly with increase in the alloying element content. The glassy rods with the maximum diameter of 5 mm can be formed in the Zr-rich region, such as $Cu_{60}Zr_{32.5}Ti_{7.5}$, $Cu_{60}Zr_{30}Ti_{10}$, $Cu_{60}Zr_{27.5}Ti_{12.5}$ and $Cu_{50}Zr_{42.5}Ti_{7.5}$, and 3 mm in the Ti-rich region, such as $Cu_{60}Zr_{15}Ti_{25}$, $Cu_{55}Zr_{10}Ti_{35}$, $Cu_{50}Zr_{10}Ti_{40}$. However, the GFA was degraded significantly in the center portion of the ternary system. For example, no BMG can be obtained for x=20-30 in $Cu_{50}Zr_{50-x}Ti_x$ and x=22.5 in $Cu_{55}Zr_{45-x}Ti_x$, and only 1 mm for x=20 in $Cu_{60}Zr_{40-x}Ti_x$, respectively. Fig. 2 shows the XRD patterns of as-cast representative alloy rods. The diffraction patterns consist only of a broad diffuse peak, suggesting a mostly

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amorphous structure.

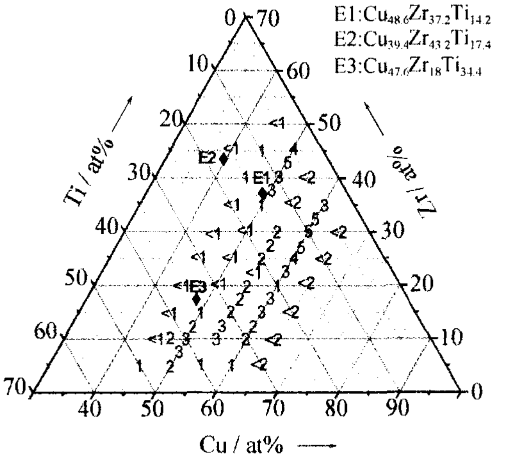

Fig. 1. Critical diameters of glass formation in ternary Cu-Zr-Ti alloy system (the eutectics are marked by E1, E2, and E3).

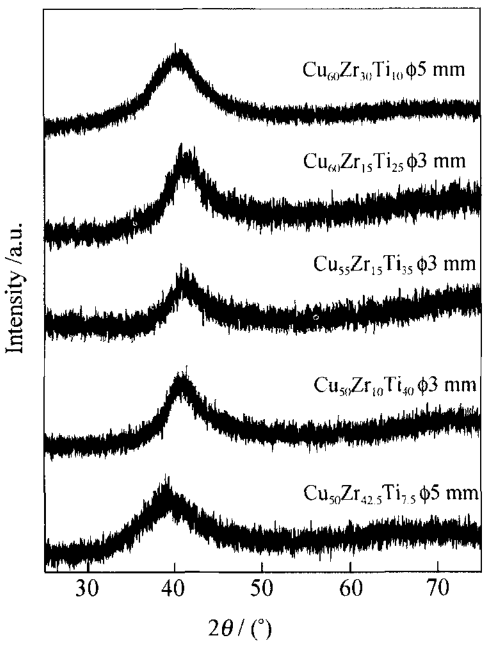

Fig. 2. XRD patterns of as-cast rods for representative ternary Cu-Zr-Ti alloys.

Fig. 3 shows the DSC curves of $Cu_{50}Zr_{50-x}Ti_x$ glassy ribbons at a heating rate of 0.67 K/s. It can be seen that crystallization modes vary from eutectic crystallization (x=0-5) to polymorphic (x=7.5-40) and then primary crystallizations (x=45) with the addition of Ti. For binary $Cu_{50}Ti_{50}$ alloy, glass transition disappears. Similar transformation of crystallization mechanism with the variation of Ti content can be observed for $Cu_{55}Zr_{45-x}Ti_x$ (Fig. 4) and $Cu_{60}Zr_{40-x}Ti_x$ [9] alloys. T_g, T_{x1} and ΔT_x are summarized in Table 1. $Cu_{50}Zr_{45}Ti_5$ glassy alloy exhibits the largest supercooled liquid temperature region of about 67 K in the Cu-Zr-Ti system.

Fig. 5 shows the melting behaviors of $Cu_{50}Zr_{50-x}Ti_x$ alloys at a heating rate of 0.067 K/s, where the apparent liquidus temperatures (T_l) are marked with arrows. The traces of x=15 and 35 show a simple melting process with one major endothermic event and a low T_l because they are close to ternary eutectics, $Cu_{48.6}Zr_{37.2}Ti_{14.2}$ and $Cu_{47.6}Zr_{18}Ti_{34.4}$, respectively. T_l of x=15 and 35 decreases dramatically by 80-110 K than the neighboring binary alloys, respectively. However, the x=25 alloy exhibits a similar major endothermic peak as well as a slightly higher T_l, about 1140 K, than the x=15 and 35 alloys. It is indicated that T_l is comparatively low for the large composition range of 15at%-35at% Ti. The reduced glass transition temperature (T_{rg}) is defined as T_g/T_l. T_l and T_{rg} are listed in Table 1. The x=15 alloy has a relatively high T_{rg}, about 0.602.

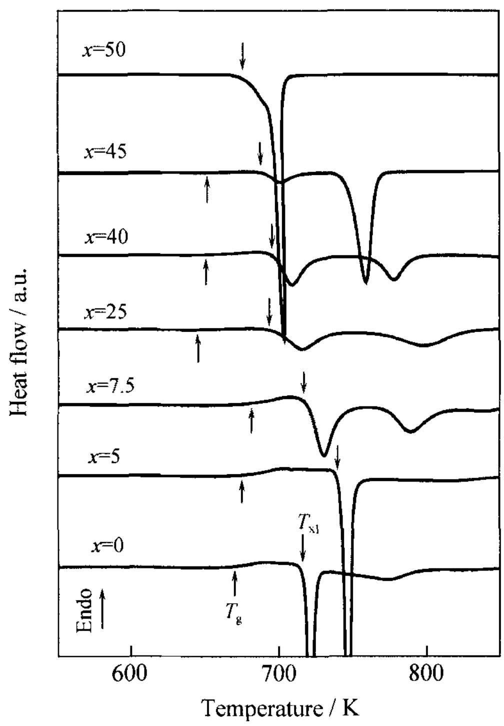

Fig. 3. DSC curves of melt-spun $Cu_{50}Zr_{50-x}Ti_x$ glassy alloys at a heating rate of 0.067 K/s.

For $Cu_{55}Zr_{45-x}Ti_x$, the x=22.5 alloy shows one major endothermic peak as well and a low T_l of about 1121 K, as shown in Fig. 6. Similarly, the x=20 alloy in $Cu_{60}Zr_{40-x}Ti_x$ exhibits a lowest T_l of about 1127 K [9].

In one word, the liquidus temperature is relatively low and flat in a broad composition region in the center portion of ternary Cu-Zr-Ti system. It is consistent with the presence of Cu_2ZrTi Laves phase in this region [10]. It is noteworthy that the composition of the Laves phase region exhibits a major endothermic peak with small temperature region and low T_l, which is similar to that of eutectic composition.

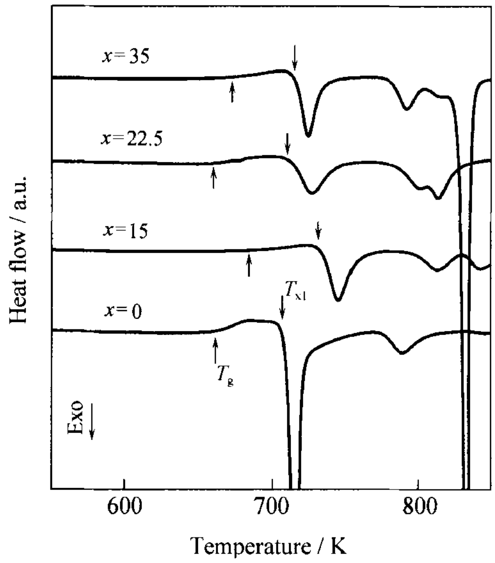

Fig. 4. DSC curves of melt-spun $Cu_{55}Zr_{45-x}Ti_x$ glassy alloys at a heating rate of 0.67 K/s.

4. Discussion

The liquidus temperature of binary Cu-Zr or Cu-Ti alloys firstly was significantly decreased with the addition of the third element, and then a series of ternary eutectics were formed in ternary Cu-Zr-Ti system, such as $Cu_{48.6}Zr_{37.2}Ti_{14.2}$ (E1), $Cu_{39.4}Zr_{43.2}Ti_{17.4}$ (E2), $Cu_{47.6}Zr_{18}Ti_{34.4}$ (E3). The ternary system exhibits lower eutectics than the corresponding binary systems, such as 1116 K for ternary eutectics $Cu_{48.6}Zr_{37.2}Ti_{14.2}$, 1158 and 1148 K for binary eutectics $Cu_{61.8}Zr_{38.2}$ and $Cu_{73}Ti_{27}$, respectively. In general, the compositions near deep eutectics or with low lying liquidus temperature have a more sluggish crystallization kinetics on cooling of the melts. Therefore, the competing crystalline phases against glass formation were suppressed and the liquidus structure of these melts can remain below glass transition temperature at a lower cooling rate. As a result, better GFA can be obtained. However, it can be found that the best glass former was not located at the eutectic composition for either Cu-Zr binary system or Cu-Zr-Ti ternary system. The GFA of binary alloys firstly was improved due to the addition of the third element, but was degraded with further increase of the third element content and even was completely destroyed in the center region, *i.e.* Laves phase region, although these compositions are near eutectics or with a low lying T_l. In another word, the eutectics in the equilibrium phase diagram did not show a good glass-forming ability in this case.

The Laves phase is present in a broad composition region in Cu-Zr-Ti system, and its structure is insensitive to composition variations. It implies that the redistribution and long range transportation of atoms is not necessary for the formation of the Laves phase on cooling. As a consequence, it nucleates and grows very easily in the undercooled liquid. It is concluded that the Laves phase is the competing crystalline phase against glass formation on cooling in the center region of the ternary diagram, and the degradation of the GFA can be attributed to the easy nucleation of the Laves phase.

Table 1. T_g, T_{x1}, T_x, T_l, T_{rg} and critical diameters of some representative glassy alloys in ternary Cu-Zr-Ti alloy system

Alloy composition / at%	T_g / K	T_{x1} / K	ΔT_x / K	T_l / K	T_{rg}	Critical diameter / mm
$Cu_{50}Zr_{50}$	670	718	48	1204	0.556	3
$Cu_{50}Zr_{45}Ti_5$	673	740	67	1165	0.578	4
$Cu_{50}Zr_{42.5}Ti_{7.5}$	677	717	40	1152	0.587	5
$Cu_{50}Zr_{40}Ti_{10}$	680	743	63	1168	0.582	3
$Cu_{50}Zr_{35}Ti_{15}$	672	705	33	1116	0.602	1
$Cu_{50}Zr_{25}Ti_{25}$	645	697	52	1140	0.566	<1
$Cu_{50}Zr_{15}Ti_{35}$	640	694	54	1134	0.564	1
$Cu_{50}Zr_{10}Ti_{40}$	652	696	44	1173	0.556	3
$Cu_{50}Zr_5Ti_{45}$	652	687	35	1212	0.538	2
$Cu_{50}Ti_{50}$	—	679	—	1248	—	<1
$Cu_{55}Zr_{30}Ti_{15}$	685	733	48	1127	0.607	2
$Cu_{55}Zr_{22.5}Ti_{22.5}$	660	712	52	1121	0.589	1
$Cu_{55}Zr_{10}Ti_{35}$	672	716	44	1172	0.573	3
$Cu_{60}Zr_{30}Ti_{10}$	713*	—	—	1151*	0.62*	5
$Cu_{60}Zr_{20}Ti_{20}$	708*	—	—	1127*	0.63*	1
$Cu_{60}Zr_{15}Ti_{25}$	688*	—	—	1213*	0.58*	3

Note: *[9].

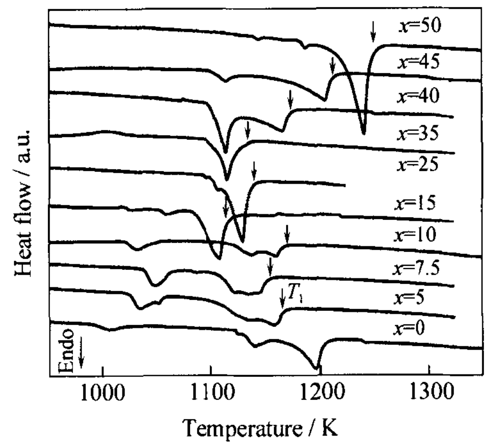

Fig. 5. DTA curves of $Cu_{50}Zr_{50-x}Ti_x$ (x=0, 5, 7.5, 10, 15, 25, 35, 40, 45 and 50) alloys at a heating rate of 0.067 K/s.

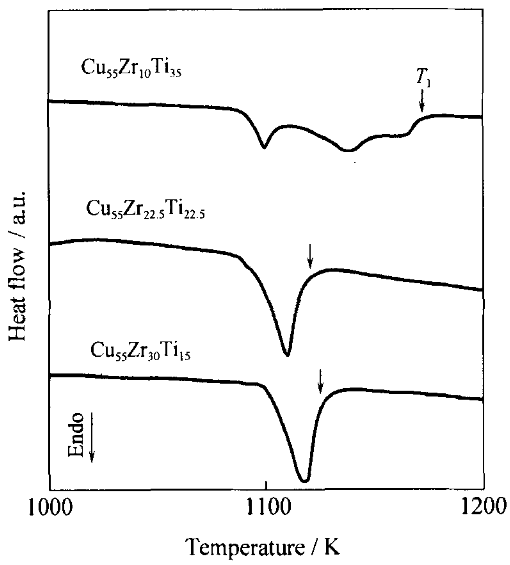

Fig. 6. DTA curves of $Cu_{55}Zr_{45-x}Ti_x$ (x=15, 22.5 and 30) alloys at a heating rate of 0.067 K/s.

5. Conclusions

Bulk metallic glass can be formed in binary Cu-Zr and ternary Cu-Zr-Ti systems by a copper mold casting method. With the addition of the third element Ti in the binary Cu-Zr system, the ternary alloys exhibit improved GFA and the glassy rods of 5 mm in diameter can be obtained. The GFA was degraded due to the presence of Laves phase in the center region of ternary phase diagram.

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