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New Ti-Based Bulk Metallic Glasses with Significant Plasticity

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Formation of Ti-based bulk metallic glasses was investigated in (Ti,Zr)–(Cu,Ni) pseudobinary system. It was found that glass-forming ability was significantly improved by the addition of Zr and Ni to the Ti–Cu binary alloys. For $Ti_{50}Zr_5Cu_{40}Ni_5$, $Ti_{45}Zr_5Cu_{45}Ni_5$, $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$ and $Ti_{42.5}Zr_{7.5}Cu_{45}Ni_5$ alloys, glassy alloy rods with diameters of 2 and 3 mm can be obtained by a copper mold casting method. The glassy alloys exhibit high compressive fracture strength of about 2 GPa, and the bulk glassy $Ti_{45}Zr_5Cu_{45}Ni_5$ alloy shows distinct plastic strain of 0.018.

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1. Introduction

Recently, Ti-based bulk metallic glasses (BMGs) have gained significant interest in basic science and engineering aspects because they have higher specific strength as compared with Pt-,[1] Zr-,[2,3] La-[4] and Cu-[5] based BMGs. Several Ti-based BMGs have been developed in Ti(–Zr)–TM–M (TM = Cu, Ni and M = Si, Sn, B, Be) alloy systems, such as Ti–Cu–Ni–B–Si–Sn,[6] Ti–Zr–Ni–Cu–Sn,[7] Ti–Zr–Ni–Cu–Be[8] and Ti–Zr–Hf–Cu–Ni–Si,[9] for which the critical diameters for glass formation range from 1 to 6 mm by an injection casting method. It assumes that the metalloid elements or beryllium are crucial for formation of the Ti-based BMG because they act as a main component with large atomic size difference and negative heats of mixing against other components in Ti–TM–M systems.[10,11] Up to date, no BMG has been produced in the Ti-based alloy systems absent from the M elements. However, addition of M elements is disadvantageous for the application of Ti-based glassy alloys due to embrittleness or potential detriment to health as biomaterials. In an unconfined geometry, failure of the Ti-based BMGs tends to occur without global plasticity. In this paper we present that Ti-based BMGs with diameters of 2 and 3 mm can be formed in (Ti,Zr)–(Cu,Ni) pseudobinary alloy system by copper mold casting, and these glassy alloys exhibit high fracture strength and significantly improved ductility.

2. Experiments

The glass-forming ability (GFA) of binary Ti–Cu, ternary Ti–Zr–Cu and quaternary Ti–Zr–Cu–Ni alloys was investigated. Alloy ingots were prepared by arc melting the mixtures of the pure elements (the purities of Ti, Zr, Cu and Ni are 99.5, 99.8, 99.95 and 99.98 mass%, respectively) under an argon atmosphere. Cylindrical rods with diameters of 1 to 4 mm were prepared from the ingots by injection casting into copper mold. Ribbon samples with a cross section of $0.02 \times 2\,mm^2$ were prepared by the melt spinning technique. Glassy structure was examined by X-ray diffraction (XRD) using Cu-Kα radiation. Thermal analysis was performed with a differential scanning calorimeter (DSC) at a heating rate of 0.67 K/s. Cylindrical rods ($\phi 2\,mm \times 4\,mm$) were used to measure compressive mechanical properties at room temperature with an Instron-type testing machine at a strain rate of $4.0 \times 10^{-4}\,s^{-1}$.

3. Results and Discussion

Formation of glassy rod with a diameter of 1 mm for binary Ti–Cu alloys by copper mold casting was unsuccessful. Nevertheless, the GFA of Ti–Cu alloys was significantly enhanced by the addition of Zr and glassy rods can be formed for the Ti–Zr–Cu alloys. The maximum diameters for glass formation were 1 mm for $Ti_{50}Zr_5Cu_{45}$, 2 mm for $Ti_{45}Zr_5Cu_{50}$, $Ti_{42.5}Zr_{10}Cu_{47.5}$ and $Ti_{37.5}Zr_{12.5}Cu_{50}$, and 3 mm for $Ti_{42.5}Zr_{7.5}Cu_{50}$ and $Ti_{40}Zr_{10}Cu_{50}$. The addition of Ni further improved the GFA of the Ti-rich alloys in the Ti–Zr–Cu system. The critical diameter increases to 2 mm with substitution of Ni for 5% Cu in $Ti_{50}Zr_5Cu_{45}$ alloy, and reduces to 1 mm with a further increase in Ni content to 7.5% (Table 1). Moreover, the critical diameter further increases to 3 mm for $Ti_{45}Zr_5Cu_{45}Ni_5$. Figure 1 shows XRD patterns of the as-cast $Ti_{50}Zr_5Cu_{40}Ni_5$ (d = 2 mm), $Ti_{45}Zr_5Cu_{45}Ni_5$ (d = 3 mm), $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$ (d = 2 mm) and $Ti_{42.5}Zr_{7.5}Cu_{45}Ni_5$ (d = 3 mm) rods, where d denotes the critical

Table 1 Critical diameters and maximum stresses of Ti-based bulk glassy alloys.

Alloys	Critical diameter (mm)	σ_f (MPa)
$Ti_{50}Zr_5Cu_{45}$	1	—
$Ti_{50}Zr_5Cu_{42.5}Ni_{2.5}$	1	—
$Ti_{50}Zr_5Cu_{40}Ni_5$	2	2020
$Ti_{50}Zr_5Cu_{37.5}Ni_{7.5}$	1	—
$Ti_{45}Zr_5Cu_{45}Ni_5$	3	1926
$Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$	2	2115
$Ti_{42.5}Zr_{7.5}Cu_{45}Ni_5$	3	2068

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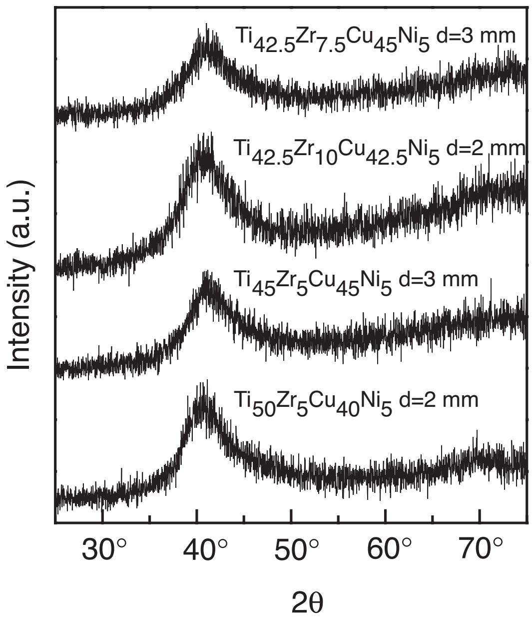

Fig. 1 XRD patterns of as-cast $Ti_{50}Zr_5Cu_{40}Ni_5$, $Ti_{45}Zr_5Cu_{45}Ni_5$, $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$ and $Ti_{42.5}Zr_{7.5}Cu_{45}Ni_5$ alloy rods.

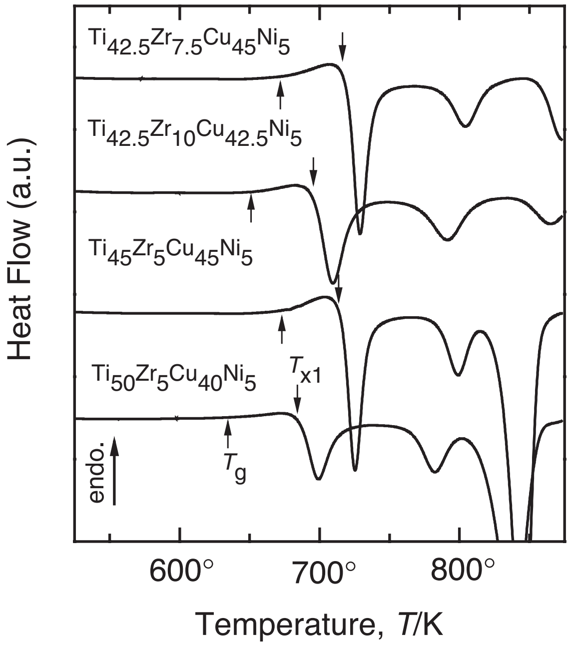

Fig. 2 DSC curves of $Ti_{50}Zr_5Cu_{40}Ni_5$, $Ti_{45}Zr_5Cu_{45}Ni_5$, $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$ and $Ti_{42.5}Zr_{7.5}Cu_{45}Ni_5$ glassy alloys at a heating rate of 0.67 K/s.

diameter for glass-formation. No distinct crystalline peaks are seen in the XRD patterns of the studied glassy alloys, indicating the formation of a single glassy phase without crystallinity.

Figure 2 shows DSC curves of the melt-spun $Ti_{50}Zr_5Cu_{40}Ni_5$, $Ti_{45}Zr_5Cu_{45}Ni_5$, $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$ and $Ti_{42.5}Zr_{7.5}Cu_{45}Ni_5$ glassy alloys. The glassy alloys exhibit a distinct glass transition and at least three crystallization peaks, followed by multiple melting processes (unshown here). The glass transition (T_g), onset temperature of first crystallization (T_{x1}) and supercooled liquid temperature

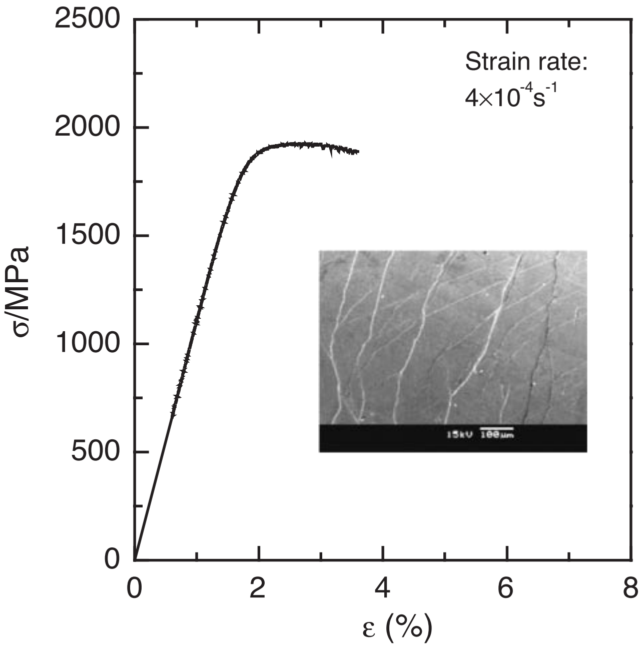

Fig. 3 Nominal compressive stress-strain curve of bulk glassy $Ti_{45}Zr_5Cu_{45}Ni_5$ alloy. The inset shows the SEM image of a lateral surface of the sample subjected to 1.8% plastic deformation.

region before crystallization ($\Delta T_x = T_{x1} - T_g$) are 634, 685 and 51 K, respectively, for $Ti_{50}Zr_5Cu_{40}Ni_5$, 673, 715 and 43 K, respectively, for $Ti_{45}Zr_5Cu_{45}Ni_5$, and 651, 695 and 45 K, respectively, for $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$. The liquidus temperature (T_l) and reduced glass transition temperature ($T_{rg} = T_g/T_l$) are 1155 K and 0.55, respectively, for $Ti_{50}Zr_5Cu_{40}Ni_5$, 1203 K and 0.56, respectively, for $Ti_{45}Zr_5Cu_{45}Ni_5$, and 1213 K and 0.54, respectively, for $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$.

Figure 3 shows the compressive stress-strain curve of the bulk $Ti_{45}Zr_5Cu_{45}Ni_5$ glassy alloy. It exhibits high maximum strength of 1926 MPa, Young's modulus of 110 GPa and distinct plastic strain to failure of 1.8%. Well-developed vein patterns on the fracture sample surfaces after compressive test could be seen by SEM, indicating the ductile feature of the glassy alloy. A number of shear bands, consisting of primary and secondary shear bands, can be observed on this sample, as depicted in the inset of Fig. 3. The secondary shear bands form at an angle of about 45° with respect to the primary shear bands, which are declined by about 45° to the compression axis. The large plasticity of the glassy alloy is attributed to a high density of shear bands formed during the compressive deformation.[1] In addition, the compressive fracture strength of $Ti_{50}Zr_5Cu_{40}Ni_5$, $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$ and $Ti_{42.5}Zr_{7.5}Cu_{45}Ni_5$ BMGs are 2020, 2115 and 2068 MPa, respectively.

It is well known that usually the alloys with high GFA are those of compositions close to the eutectic points. However, the present study indicated that in the Ti-rich region of Cu–Zr–Ti system, the $Ti_{42.5}Zr_{7.5}Cu_{50}$ and $Ti_{40}Zr_{10}Cu_{50}$ alloys, which are far away from the eutectic composition $Ti_{34.4}Zr_{18}Cu_{47.6}$,[12] exhibited the highest GFA and the glassy rods with diameters up to 3 mm were obtained. The critical diameter was only 1 mm for the $Ti_{35}Zr_{15}Cu_{50}$ alloy, which is close to the eutectics. It is considered that these results concerning the GFA of the Cu–Zr–Ti alloys are attributed to the existence of the CuZrTi Laves phase region near the $Ti_{34.4}Zr_{18}Cu_{47.6}$ eutectics.[12,13] Although the Laves phase has a relatively low liquidus temperature, it is nonstoichiometric and the structure is insensitive to the variations of composition, so that it nucleates more easily than other competing phases during solidification. In other words, the Laves phase is the competing phase with respect to glass formation on cooling the melt and the alloys with compositions in or close to the region of the Laves phase have relatively low GFA. We suggest that the alloys with high GFA should be close to the compositions, including some deep eutectics, at which the structure is sensitive to composition variations.

On the other hand, although the $Ti_{50}Cu_{50}$ alloy has the highest liquidus temperature in the local composition in Ti-Cu binary alloy system and only glassy ribbon can be obtained, the GFA was significantly improved by the addition of Zr and Ni. With the addition of Zr, the critical diameter increased to 1 mm for $Ti_{50}Zr_5Cu_{45}$, and 2 mm for $Ti_{45}Zr_5Cu_{50}$, and further 3 mm for $Ti_{42.5}Zr_{7.5}Cu_{50}$ and $Ti_{40}Zr_{10}Cu_{50}$. With the addition of Ni, the critical diameter increased to 2 mm for $Ti_{50}Zr_5Cu_{40}Ni_5$ and 3 mm for $Ti_{45}Zr_5Cu_{45}Ni_5$ alloys. This is attributed to the reduction of the liquidus temperature of the alloys with the partial substitution of Zr or Ni for Ti or Cu in the $Ti_{50}Cu_{50}$ alloy. For example, the liquidus temperature is 1249 K for $Ti_{50}Cu_{50}$, and decreases to 1213 and 1173 K for $Ti_{45}Zr_5Cu_{50}$ and $Ti_{40}Zr_{10}Cu_{50}$, and 1203 and 1155 K for $Ti_{45}Zr_5Cu_{45}Ni_5$ and $Ti_{50}Zr_5Cu_{40}Ni_5$, respectively. It is implied that the addition of Zr and Ni to the Ti–Cu alloy stabilizes the undercooled liquid of the alloys. Mainly, the strong interactivity and atomic size mismatches between Ti and Ni and between Cu and Zr is responsible for the stabilization of the undercooled liquids now that Ti and Zr, as well as Cu and Ni, are interchangeable from the point of view of chemistry and there are large negative heat of mixing of -23 kJ/mol and -35 kJ/mol for the atomic pairs of Cu–Zr and Ti–Ni, respectively.[14]

4. Conclusions

In summary, the GFA of Ti–Cu binary alloys was significantly improved by the addition of Zr (5–12.5 at.%) and/or Ni (5 at.%) mainly because of the strong interactivity and significant atomic size mismatches between Ti and Ni and between Cu and Zr, but is degraded with further increase in the contents of Zr or Ni due to the easy crystallization of Laves phase on cooling the melts. The critical diameters for glass formation are 2 mm for $Ti_{50}Zr_5Cu_{40}Ni_5$ and $Ti_{42.5}Zr_{10}Cu_{42.5}Ni_5$ alloys, and 3 mm for $Ti_{45}Zr_5Cu_{45}Ni_5$ and $Ti_{42.5}Zr_{7.5}Cu_{45}Ni_5$ alloys. The bulk glassy $Ti_{45}Zr_5Cu_{45}Ni_5$ alloy exhibits high maximum compressive strength of 1926 MPa and large global plasticity of 1.8%.

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