Precipitation of Icosahedral Phase in Zr-Ni-Nb-Cu-Al Metallic Glasses

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The crystallization behaviors of Zr-Ni-Nb-Cu-Al metallic glasses are greatly influenced by the substitution of Ni for Zr. For the glassy Zr_{71-x}Ni_{10-x}Nb_{16}Cu_{10}Al_{10} (x = 7, 9, 11 at%) alloys, the onset temperature of crystallization \( T_x \) increases from 717 to 748 K with increasing Ni content from 7 at% to 11 at%. The primary crystallization reaction of the studied glassy alloys corresponds to the formation of icosahedral phase from amorphous matrix. The precipitation of quasicrystalline phase with a large volume fraction in the Zr_{65}Ni_{10}Nb_{16}Cu_{10}Al_{10} alloy indicates that the decrease of Ni content promotes the formation of icosahedral phase. Johnson-Mehl-Avrami analysis of isothermal transformation data suggests that the icosahedral phase precipitation proceeds by a diffusion-controlled growth mode with nearly constant nucleation rate.

Furthermore, the Zr_{71-x}Ni_{10-x}Nb_{16}Cu_{10}Al_{10} (x = 7, 9, 11 at%) alloys possess high glass-forming ability, and the critical diameter for glass formation reaching 6 mm, 9 mm and 9 mm by copper-mould casting method, respectively. [doi:10.2320/matertrans.M2009072]

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1. Introduction

The nature of the short-range order of metallic liquids and glasses is of fundamental interest, and an icosahedral short-range order (ISRO) has been suggested as the intrinsic local structure of metallic liquids and glasses.\(^1\)\(^-\)\(^5\) The diffraction patterns of icosahedral symmetry discovered by Schechtman et al.\(^5\) in rapidly quenched Al-Mn alloy. Since then, in a variety of amorphous alloy systems, such as Pd\(_{60}\)U\(_{20}\)Si\(_{20}\),\(^7\) Al\(_{55}\)Mn\(_{20}\)Si\(_{25}\),\(^8\) Al\(_{65}\)Cu\(_{20}\)Fe\(_{15}\)\(^9\) and Ti\(_{33}\)Zr\(_{27}\)Ni\(_{20}\)\(^10\) amorphous ribbons, it has been demonstrated that icosahedral quasicrystalline phase (I-phase) can be synthesized by crystallization from amorphous state. Recent researches reveal that the icosahedral phase has been observed in a number of Zr-based metallic glasses with high glass-forming ability (GFA) during early stage of crystallization.\(^11\)\^-\(^22\)

Köster et al. reported the formation of I-phase upon crystallization in Zr-Cu-Al\(^1\) and Zr-Cu-Ni-Al\(^11\)-\(^14\) metallic glasses. Icosahedral phase formation in some of these alloys is attributed to the presence of oxygen impurity.\(^13\),\(^15\) Very recently, it has been reported that the addition of the noble elements, such as Ag, Pd, Pt and Au, caused I-phase formation from the amorphous state in Zr-Al-Ni-Cu, Zr-Al-Ni and Zr-TM (TM = Fe, Ni, Co, Cu) alloy systems.\(^16\)\^-\(^19\) The formation of I-phase was also found in Zr-Al-Ni-Cu glassy alloys containing transition metals Nb, Ta, V or Mo.\(^20\),\(^21\) The results indicate that the ISRO is strengthened in Zr-based glasses by the presence of additional alloying elements, as well as oxygen impurity. However, the addition of oxygen, noble metals and transition metals reduced the GFA of these Zr-based alloys, which could be due to the heterogeneous nucleation induced by O addition,\(^23\) deviation of the alloy compositions from the best glass-forming compositions by the minor alloy additions.\(^22\)\(^\)\^-\(^23\) etc.

Recently, we have developed a new family of Zr-based metallic glasses in Zr-Ni-Nb-Cu-Al system, which not only can precipitate I-phase upon crystallization but also have high GFA. This paper presents the formation of I-phase in the Zr\(_{71-x}\)Ni\(_{10-x}\)Nb\(_{16}\)Cu\(_{10}\)Al\(_{10}\) (x = 7, 9, 11 at%) glassy alloys and the kinetic behavior of quasicrystal formation from amorphous state. The glass-forming ability of the studied alloys is also presented.

2. Experimental Procedures

Alloy ingots with nominal compositions of Zr\(_{71-x}\)Ni\(_{10-x}\)Nb\(_{16}\)Cu\(_{10}\)Al\(_{10}\) (x = 7, 9, 11 at%) were prepared by arc-melting the mixture of the pure metals Zr, Ni, Nb, Cu and Al in a Ti-gettered argon atmosphere. From the master alloys, ribbons and cylindrical rods were prepared by single-roller melt spinning and copper mold casting, respectively, in an argon atmosphere. The structure of the samples was examined by X-ray diffraction (XRD) using a Bruker AXS D8 X-ray diffractometer with Cu-K\(\alpha\) radiation. Thermal analysis experiments were performed by using a NETZSCH DSC 404 C differential scanning calorimeter (DSC) at a heating rate of 0.33 Ks\(^{-1}\) under a flowing purified argon atmosphere. The glassy ribbons were annealed to crystallization in the DSC cell at a heating rate of 0.33 Ks\(^{-1}\), and then cooled to room temperature. Structure changes after heat treatment of amorphous ribbons were studied by using XRD and a JEM2100F transmission electron microscopy (TEM), operated at the acceleration voltage of 200 kV. The samples for TEM were the ribbons that were thinned electrochemically by jet polishing at 263 K with 20 V, using a solution of CH\(_3\)OH and HNO\(_3\) in the volume ratio of 2 : 1.

3. Results and Discussion

Figure 1 shows DSC curves of melt-spun Zr\(_{71-x}\)Ni\(_{10-x}\)Nb\(_{16}\)Cu\(_{10}\) (x = 7, 9, 11 at%) glassy alloys. The metallic glasses exhibit distinct glass transition, followed by the appearance of a wide supercooled liquid region, multiple stage crystallization and then melting behaviors. The glass transition temperature (\( T_g \)), the onset temperature of crystallization (\( T_x \)), the onset melting temperature (\( T_m \)) and the liquidus temperature (\( T_l \)) are shown in the DSC traces. Three-stage exothermic reactions are observed in all the studied
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The crystallization behaviors of melt-spun Zr$_{71-x}$Ni$_x$Nb$_3$Cu$_{16}$Al$_{10}$ ($x=7, 9, 11$ at%) glassy alloys were examined. Figure 2 shows the X-ray diffraction patterns of the heat-treated Zr$_{64}$Ni$_7$Nb$_3$Cu$_{16}$Al$_{10}$ samples. Figure 2(a) corresponds to the specimen heated to 717 K. It shows some sharp diffraction peaks which are identified corresponding to an I-phase. The indexing of the peaks was carried out on the basis of six independent Miller indices proposed by Bancel et al. The crystallization product of the sample heated to 739 K (i.e. the completion of the first exothermic reaction) is similar to that heated to 717 K, as shown in Fig. 2(b). This result clarifies that the crystalline phase of the first peak is a single I-phase. After heating through the second exothermic peak (Fig. 2(c)), the XRD pattern exhibits some Bragg peaks that are indexed to tetragonal Zr$_2$Ni, tetragonal CuZr$_2$ and face-centered-cubic Zr$_2$Ni (FCC-Zr$_2$Ni) phases. The low-intensity peaks of FCC-Zr$_2$Ni phase indicate a small volume fraction of the phase. This reveals that the second exothermic reaction corresponds to decomposition of the initial I-phase.

Upon heating to 973 K, the major crystalline phases in Zr$_{62}$Ni$_9$Nb$_3$Cu$_{16}$Al$_{10}$ alloy are tetragonal Zr$_2$Ni, tetragonal CuZr$_2$ and hexagonal Zr$_6$NiAl$_2$ phases (Fig. 2(d)).

The XRD patterns for the heat-treated Zr$_{62}$Ni$_9$Nb$_3$Cu$_{16}$Al$_{10}$ glass alloys are shown in Fig. 3. The XRD pattern of the sample heated to 738 K shows sharp diffraction peaks, which can be indexed to an I-phase, in addition to a halo peak corresponding to the residual glassy phase (Fig. 3(a)). As shown in Fig. 3(b), after heating through the second exothermic peak, tetragonal Zr$_2$Ni, tetragonal CuZr$_2$ and FCC-Zr$_2$Ni phases are observed. The XRD pattern of the specimen heated to 1023 K indicates it is consisted of two crystalline phases of tetragonal CuZr$_2$ and tetragonal Zr$_2$Ni structures (Fig. 3(c)). The crystallization process and products of the 11 at% Ni-containing alloy are similar to that of Zr$_{62}$Ni$_9$Nb$_3$Cu$_{16}$Al$_{10}$.

As mentioned above, the first exothermic peaks of Zr$_{71-x}$Ni$_x$Nb$_3$Cu$_{16}$Al$_{10}$ ($x=7, 9, 11$ at%) alloys correspond to the reaction of the primary I-phase precipitation from amorphous matrix. The larger area of the first peak of Zr$_{64}$Ni$_7$Nb$_3$Cu$_{16}$Al$_{10}$ alloy compared with that of Zr$_{71-x}$Ni$_x$Nb$_3$Cu$_{16}$Al$_{10}$ ($x=9, 11$ at%) alloys indicates that Ni content has a distinct effect on the precipitation of I-phase in Zr-Ni-Nb-Cu-Al metallic glasses and the decrease of Ni content enhances the formation of I-phase from amorphous structure. Previous studies revealed that the icosahedral-like local structure is the dominant local structure in Zr-based glass alloys with high glass-forming ability. The precipitation of icosahedral quasicrystal as the initial crystalline phase in this study strongly supports the existence of icosahedral short- or medium-range order in Zr-Ni-Nb-Cu-Al glassy alloys.

![Fig. 1 DSC curves of Zr$_{71-x}$Ni$_x$Nb$_3$Cu$_{16}$Al$_{10}$ ($x=7, 9, 11$ at%) melt-spun ribbons.](image1)

![Fig. 2 X-ray diffraction patterns of Zr$_{64}$Ni$_7$Nb$_3$Cu$_{16}$Al$_{10}$ ribbons heated to (a) 717 K, (b) 739 K, (c) 783 K and (d) 973 K.](image2)

![Fig. 3 X-ray diffraction patterns of Zr$_{62}$Ni$_9$Nb$_3$Cu$_{16}$Al$_{10}$ ribbons heated to (a) 738 K, (b) 783 K and (c) 1023 K.](image3)
For further confirming the icosahedral quasicrystalline phase, we investigated the microstructure of the samples by TEM. Figure 4 shows the bright-field electron micrograph and electron diffraction patterns of $\text{Zr}_{64}\text{Ni}_{7}\text{Nb}_{3}\text{Cu}_{16}\text{Al}_{10}$ glassy alloys heated up to 717 K. The annealed specimen shows a fine-grained microstructure with typical grain size of about 200 nm. The electron diffraction patterns in Figs. 4(b), (c) and (d) show five-fold, three-fold and two-fold rotation symmetries, respectively, which are characteristic of I-phase. Figure 5(a) shows the high resolution electron image of one particle with the five-fold zone axis parallel to the electron beam incidence. Figure 5(b) is the fast Fourier transform of
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The research in the present study reveals that icosahedral order exists in Zr-Ni-Nb-Cu-Al metallic glasses. The similar results have also been reported in other researches. It is suggested that icosahedral clusters exist in the molten alloy and remain in the rapid-solidified glassy alloy. The icosahedral clusters could restrain the crystallization of the molten alloy during rapid solidification, which is a dominant factor for the high GFA. The icosahedral phase may precipitate by the slight deviation of the alloy composition from that with the highest GFA. The results, as mentioned above, indicate that the I-phase formation is enhanced with the decrease of Ni content but the GFA is reduced. The deviation from the alloy composition with the highest GFA may be the origin for the fact.

4. Conclusions

A transformation from glassy structure to an icosahedral phase was found in Zr_{71-x}Ni_{Nb}{Cu}{16}{Al}_{10} (x = 7, 9, 11 at%) glassy alloys upon crystallization. The first crystallization reaction of the studies glassy alloys correspond to the formation of I-phase. The formation of quasicrystalline phase with a larger volume fraction in Zr_{64}Ni_{3}Cu_{16}Al_{10} alloy indicates that the decreasing of Ni content can stabilize the icosahedral structure. The JMA analysis of isothermal transformation data suggests that the icosahedral phase crystallization proceeds by a diffusion-controlled growth mode at nearly constant nucleation rate. The critical diameters for glass formation of Zr_{71-x}Ni_{Nb}{Cu}{16}{Al}_{10} (x = 7, 9, 11 at%) alloys are 6 mm, 9 mm and 9 mm, respectively.

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REFERENCES


Fig. 6 Replots of isothermal DSC traces into a form of ln(ln(1/1 − x)) against ln(t − τ).
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