Nano Icosahedral Quasicrystalline Phase in $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ Quaternary Glassy Alloy

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A nano icosahedral quasicrystalline phase was confirmed as the primary precipitation phase in the melt-spun $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ quaternary glassy alloy with a two-stage crystallization process. The onset temperature of the first exothermic peak is 704 K at a heating rate of 0.67 K s^{-1} . Although no significant X-ray diffraction peaks were observed in the sample annealed at 705 K, we confirmed the formation of the icosahedral phase by nano beam electron diffraction using FE-TEM. The icosahedral particles have an extremely fine grain size in the diameter range of 2 to 4 nm. In addition to the icosahedral phase, the nano crystalline particles corresponding to Zr_2Ag and/or fcc- Zr_2Ni structures are also observed in the annealed sample. The second exothermic peak denotes the transition from the nano icosahedral to the crystalline phase of Zr_2Ag , fcc- Zr_2Ni and Zr_4Al_3 . The formation of the nano icosahedral phase as the primary phase is due to a high nucleation rate and strongly implies the existence of an icosahedral short-range order in the glassy state.

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1. Introduction

Since the reproducible formation of the nano icosahedral quasicrystalline phase as a primary precipitation phase in the $\text{Zr-Al-Ni-Cu-NM}^{1,2)}$ ($\text{NM} = \text{Ag, Pd, Au, Pt}$) and $\text{Zr-Al-Ni-M}^{3)}$ ($\text{M} = \text{Pd, Au, Pt}$) multicomponent glassy alloys with high glass-forming abilities was reported, it has been found that addition of a noble metal is effective for icosahedral phase formation in Zr-based alloys.⁴⁻⁸⁾ We suggested that the icosahedral cluster exists in the Zr-based glassy alloy, and noble metal plays a significant role in increasing the nucleation rate resulting from the enhancement of the precipitation phase with an icosahedral structure.^{9,10)} These suggestions also imply a structural correlation between a high glass-forming ability and icosahedral atomic configurations. Recently, we reported an icosahedral medium-range order in the melt-spun $\text{Zr}_{70}\text{Pd}_{30}$ glassy alloy using a high-resolution transmission electron microscope (HREM) and nano beam diffraction analysis.¹¹⁾ Moreover, a similar ordered region has been observed in the $\text{Zr}_{54.5}\text{Ti}_{7.5}\text{Cu}_{20}\text{Ni}_8\text{Al}_{10}$ multicomponent glassy alloy, where the icosahedral phase is formed at a low cooling rate.¹²⁾ These results suggest that Zr-based glassy alloys contain an icosahedral short- and/or medium-range order in a glassy state, which stabilizes the glassy state by suppressing the rearrangement of constitutional elements to form the crystalline phase. Although the icosahedral phase is expected to be formed in the Zr-Al-Ni-Ag quaternary glassy alloy, its formation has not been confirmed because of the extremely fine grain size of the primary phase in comparison with those in the Pd-, Au- and Pt-containing alloys. In this paper, we report the formation of an icosahedral phase with an extremely fine grain size in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ glassy alloy analyzed by HREM observation and nano beam diffraction using the field-emission transmission electron

microscopy (FE-TEM).

2. Experimental Procedure

A melt-spun $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ ribbon sample with a cross section of $0.03 \times 1 \text{ mm}^2$ was produced from an alloy ingot prepared by arc melting high-purity metals of 99.8 mass%Zr, 99.99 mass%Al, 99.9 mass%Ni, 99.99 mass%Cu and 99.9 mass%Ag in a purified argon atmosphere. Thermal properties were measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 K s^{-1} . The annealed structure was examined by X-ray diffractometry with $\text{Cu-K}\alpha$ radiation and FE-TEM with an accelerating voltage of 300 kV (JEOL JEM-3000F).

3. Results and Discussion

Figure 1 shows a DSC curve of the melt-spun $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ ribbon. Two exothermic reactions are

Fig. 1 DSC curve of a melt-spun $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ glassy alloy.

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Fig. 2 X-ray diffraction pattern of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ glassy alloy annealed for 600 s at 705 K.

observed followed by the glass transition. The glass transition temperature, T_g and the onset temperature, T_x of the lower exothermic peak are 671 K and 704 K, respectively. It is shown that the first exothermic peak is weak and broad compared with those in the Zr–Al–Ni–(Pd, Au and Pt) glassy alloys. The temperature gap between the two exothermic peaks is 72 K, which is significantly smaller than that (118 K) in the Zr–Al–Ni–Pd alloy and nearly equal to those of the Zr–Al–Ni–Au (73 K) and Zr–Al–Ni–Pt (81 K) alloys.³⁾

In order to identify the precipitation phase formed by the first broad exothermic reaction, we examine the X-ray diffraction (XRD) pattern of the sample heated for 600 s at 705 K shown in Fig. 2. No obvious crystalline reflections are observed even in the annealed state, implying the formation of extremely fine precipitates. Figure 3 shows the bright-field TEM image (a), selected-area electron diffraction pattern (b) and nano beam electron diffraction patterns ((c)–(e)) of the sample annealed for 600 s at 705 K. The beam diameters for selected-area diffraction and nano beam diffraction are 1 μm and 2.4 nm, respectively. In the bright-field image, no obvious precipitations are observed, suggesting that very fine grains exist. The selected-area electron diffraction pattern consists of broad rings and is in agreement with the XRD result. The nano beam diffraction patterns shown in Figs. 3((c)–(e)) taken from the annealed sample are identified as five-, three- and twofold symmetries, although the contrast of the diffraction patterns is weak due to the extremely fine grain size. Therefore, it is concluded that the icosahedral phase is formed in the Zr–Al–Ni–Ag quaternary alloy. We also obtained a nano beam diffraction pattern corresponding to a crystalline phase. Thus, the primary phase is recognized to be a mixture of the quasicrystalline and crystalline phases. The crystalline phase appears to be Zr_2Ag and/or fcc- Zr_2Ni . However, the details of the structure of the crystalline phase are not clear. For the identification of the precipitated grains, we performed HREM observation of the annealed sample. Figure 4 shows the high-resolution TEM image of the sample annealed for 600 s at 705 K. The precipitated grains in a diameter range of 2 to 4 nm are shown in the image. The precipitated phases have an extremely fine grain size, which implies that the icosahedral phase with Zr_2Ag and/or fcc- Zr_2Ni has a high number of nucleation sites and a low grain growth rate.

We have previously reported the effect of the addition of Ag and Pd on the precipitation behavior of the icosahedral phase in Zr-based glassy alloys.⁹⁾

The nucleation rate increases significantly from 10^{16} to $10^{20} \text{ m}^{-3} \text{ s}^{-1}$ and the grain growth rate decreases from approximately 10^{-8} to 10^{-9} m s^{-1} with the addition of 10 at% Ag or Pd in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{M}_{10}$ ($\text{M} = \text{Ag}$ or Pd) alloys. Moreover, it has been reported that the nucleation rate of the primary phase significantly increases with an increase of Pd content in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5-x}\text{Pd}_x$ ($x = 0$ to 17.5) alloys.¹³⁾ In this study, the nucleation rate is calculated to be approximately $10^{22} \text{ m}^{-3} \text{ s}^{-1}$ in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ quaternary alloy, which is 10^6 times higher than that of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ quaternary alloy and 10^2 times higher than that of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ quinary alloy. The grain growth rate of the primary phase also decreases with increasing Pd content. From these studies on the nucleation and grain growth behaviors, it is clear that noble metals effectively increase the number of the nucleation sites and suppress the grain growth. The present results also indicate that refinement of the icosahedral particle is due to the high nucleation rate resulting from the addition of large amounts of noble metal.

The size of the icosahedral phase in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Pd}_{17.5}$ quaternary alloy annealed for 30 s at 730 K (T_x) is in the range of 5 to 20 nm,¹³⁾ which is considerably larger, even with the shorter annealing time, than that of the present alloy. Pd has no chemical affinity with Ni (0 kJmol^{-1}) and large negative mixing enthalpies with Zr (-91 kJmol^{-1}) and Al (-46 kJmol^{-1}).¹⁴⁾ In contrast, Ag has a positive mixing enthalpy with Ni ($+15 \text{ kJmol}^{-1}$) and small negative enthalpies with Zr (-20 kJmol^{-1}) and Al (-4 kJmol^{-1}). Therefore, it is suggested that the glassy state of the Ag-containing alloy is much less stable than that of the Pd-containing alloy. It is realized that precipitation of the nano icosahedral phase with fine grain size results from the addition of Ag which causes deviation from the three empirical rules for a high glass-forming ability.¹⁵⁾ The formation of the nano icosahedral phase upon a significant increase in the nucleation rate also implies the existence of an icosahedral short-range order in the present glassy alloy, leading to restraint of the crystallization reaction.

Finally, we examined the transformation reaction corresponding to the second exothermic peak and thermal stability of the icosahedral phase. Figure 5 shows the X-ray diffraction pattern of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ alloy annealed for 1.8 ks at 873 K. The diffraction peaks are identified as Zr_2Ag , Zr_2Ni and Zr_4Al_3 . Neither the residual existence of the icosahedral phase nor a broad peak due to the amorphous phase is observed. The second exothermic peak is concluded to result from the transition of the icosahedral phase to the crystalline phases. The formation of the metastable nano icosahedral phase as a primary precipitation phase is in good agreement with those of other Zr-based multicomponent glassy alloys.^{1–3)}

4. Conclusions

The nano icosahedral quasicrystalline phase is identified as the primary phase in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ quaternary glassy alloy. The icosahedral particles have an extremely fine grain size in the diameter range of 2 to 4 nm. The nano crystalline particles which appear to have Zr_2Ag and/or fcc-

Fig. 3 Bright-field TEM image (a), selected-area electron diffraction pattern (b) and nano beam electron diffraction patterns (c)–(e) of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ glassy alloy annealed for 600 s at 705 K. The beam diameter is approximately 1 μm for selected-area electron diffraction and is approximately 2.4 nm for nano beam electron diffraction.

Fig. 4 High-resolution transmission electron micrograph of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ glassy alloy annealed for 600 s at 705 K.

Zr_2Ni structures are also observed. The icosahedral phase transforms to stable crystalline phases of Zr_2Ag , fcc- Zr_2Ni and Zr_4Al_3 in the second exothermic reaction. The precipitation of the icosahedral particles with a very fine grain size is due to the extremely high nucleation rate in the present alloy. The high nucleation rate is attributed to the addition of large amounts of Ag, which has a positive mixing enthalpy with Ni and weak chemical affinities with Zr and Al. The formation

Fig. 5 X-ray diffraction pattern of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Ag}_{17.5}$ glassy alloy annealed for 1.8 ks at 873 K.

of the nano icosahedral phase under a high nucleation rate strongly suggests that an icosahedral short-range order exists in the glassy state, leading to the restraint of the crystallization reaction.

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