Formation of an Icosahedral Quasicrystalline Phase in Zr_{65}Al_{17.5}Ni_{10}M_{17.5} (M = Pd, Au or Pt) Alloys

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An icosahedral (I) phase was found to be formed as a metastable phase in the crystallization process of amorphous Zr_{65}Al_{17.5}Ni_{10}M_{17.5} (M = Pd, Au or Pt) alloys. The three amorphous alloys show an endothermic reaction due to the glass transition, followed by two exothermic peaks. The first exothermic peak is due to the precipitation of an I-phase and the second one results from the transition from the I to crystalline mixed phases of ZrAl\textsubscript{5} + ZrNi + ZrPt (Zr_{2}Au or ZrPd). The I-phase consists of fine grains with a size of about 10 nm and no distinct residual amorphous phase is seen. The formation of the I-phase in the new Zr-based alloy systems with a large supercooled liquid region and high glass-forming ability is important for the future development of bulk quasicrystalline alloys as basic science and engineering materials.

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1. Introduction

It is known that metallic alloys are composed only of three types of structures, \textit{i.e.}, crystalline, amorphous and quasicrystalline. The alloy systems in which the quasicrystalline phase is formed have been limited to Al-, Mg-, Ga-, Zn- and Ti-based systems.\textsuperscript{1,2} Recently, it has been reported that the icosahedral (I) phase is also formed in the crystallization process of Zr-Al-Ni-Cu\textsuperscript{3} and Zr-Ti-Al-Ni-Cu\textsuperscript{5} alloys containing oxygen as an impurity element. However, no subsequent data on the formation of the I-phase in the Zr-Al-Ni-Cu alloys had been presented by the other groups because of the difficulty of controlling oxygen content. More recently, the intentional addition of oxygen to Zr-Al-Cu alloys has been confirmed to cause an easy precipitation of the I-phase during crystallization.\textsuperscript{5} The existence of oxygen in the Zr-based amorphous alloys is harmful for the achievements of high glass-forming ability (GFA) and good mechanical properties. It is therefore important to find a Zr-based amorphous alloy in which the I-phase is formed as a primary precipitation phase even in the absence of intentional oxygen addition. We have reported that the addition of Ag,\textsuperscript{6} Pd,\textsuperscript{7} Au\textsuperscript{8} or Pt\textsuperscript{9} to the Zr-Al-Ni-Cu alloys causes a reproducible precipitation of the I-phase from the amorphous phase. The I-phase has a nanoscale particle size less than 40 nm and disperses isolatedly in an amorphous matrix. The formation of the nanostructure has enabled us to maintain a good ductility even for the I-based alloys.\textsuperscript{7,8,9,10} This result indicates the possibility that a new type of high-strength alloy is developed by utilizing the phase transformation to the I-phase. Although the formation of the I-phase from an amorphous phase has been reported in Pd-U-Si\textsuperscript{11} and Al-Cu-V\textsuperscript{12} alloys, these alloys are extremely brittle in the amorphous and crystalline states, being completely different from the good ductile nature for the Zr-Al-Ni-Cu-M (M = Ag, Pd, Au or Pt) alloys. It is also known that the Zr-based amorphous alloys have a large supercooled liquid region before crystallization and a high GFA leading to the formation of bulk amorphous alloys.\textsuperscript{7,9,11} That is, the use of the Zr-based alloys has resulted in the formation of bulk I-based alloys with the good ductility. The good ductility in the I-based alloys has been presumed to be related to the precipitation of the I-phase from the supercooled liquid.\textsuperscript{9,10} It is therefore important to search for a new bulk amorphous alloy system in which an I-phase is formed from the supercooled liquid region. In the subsequent research, we have found that an I-phase precipitates as a primary phase from the supercooled liquid in amorphous Zr_{65}Al_{17.5}Ni_{10}M_{17.5} (M = Ag, Pd, Au or Pt) alloys. This paper is intended to present the precipitation of the I-phase in the amorphous Zr-based alloys containing Pd, Au or Pt and to investigate the reason for the formation of the I-phase.

2. Experimental Procedure

Quaternary alloy ingots with composition of Zr_{65}Al_{17.5}Ni_{10}M_{17.5} (M = Pd, Au or Pt) were prepared by arc melting the mixtures of pure metals of 99.8 mass\%Zr including impurities of \textasciitilde 320 mass ppm O, 211 mass ppm Fe, 44 mass ppm Hf and 35 mass ppm Cr. 99.99 mass\% Al, 99.9 mass\% Ni and above 99.9 mass\% M (M = Pd, Au or Pt) in an argon atmosphere. The compositions represent nominal atomic percentages. Amorphous alloy ribbons with a cross section of 0.02 ×1 mm\textsuperscript{2} were produced by melt spinning in an argon atmosphere. The amorphous structure was examined by X-ray diffraction and transmission electron microscopy (TEM). The thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s, X-ray diffraction and TEM linked with nanobeam electron diffraction. Nanobeam electron diffraction patterns were taken from the small region of 2.4 nm in diameter.
3. Results

The X-ray diffraction patterns of the melt-spun Zr_{65}Al_{17.5}Ni_{10}M_{17.5} (M = Pd, Au or Pt) alloys consisted only of broad peaks. Neither crystalline reflection spots in the electron diffraction patterns nor crystalline contrast in the bright-field TEM image were seen for all the alloys, indicating that an amorphous single phase is formed in the three alloys. Figure 1 shows DSC curves of the amorphous Zr-based alloys containing Pd, Au or Pt. The DSC curves show an endothermic reaction as marked with glass transition (T_g), followed by two exothermic peaks, indicating that the crystallization reaction occurs through two stages from the supercooled liquid. In order to examine the precipitation phase caused by the first-stage exothermic reaction, the X-ray diffraction patterns of the three alloys heated for 60 s at each onset temperature (T_s) of the first exothermic reaction are shown in Figure 2.

![DSC curves](image)

**Fig. 1** DSC curves of melt-spun Zr_{65}Al_{17.5}Ni_{10}M_{17.5} (M = Pd, Au or Pt) amorphous alloys. The T_g and T_s represent the onset temperatures of the endothermic reaction and the first-stage exothermic reaction, respectively.

![X-ray diffraction patterns](image)

**Fig. 2** X-ray diffraction patterns of melt-spun Zr_{65}Al_{17.5}Ni_{10}M_{17.5} (M = Pd, Au or Pt) amorphous alloys annealed for 60 s at each T_s.

![Bright-field TEM image](image)

**Fig. 3** Bright-field TEM image (a), selected-area electron diffraction pattern (b) and nanobeam electron diffraction patterns (c) to (e) of the Zr_{65}Al_{17.5}Ni_{10}Pd_{17.5} amorphous alloy annealed for 60 s at 730 K.
Fig. 2. All the diffraction patterns are in a superimposed state of broad halo peaks and some sharp peaks with higher intensities. As identified in the figure, all the sharp peaks are identified as an I-phase. Figures 3 and 4 show bright-field TEM images, selected-area electron diffraction patterns and nanobeam electron diffraction patterns of the Zr-based alloys containing Pd or Au, respectively, subjected to the same annealing treatment as that in Fig. 2. Both the alloys consist of fine grains with a size of about 10 nm and no distinct residual amorphous phase is observed in the TEM images judging from nano granular image contrast. The ordinary electron diffraction patterns consist of some reflection rings which can be identified as an I-phase. The nanobeam diffraction patterns are also identified as five-, three- and two-fold symmetries of the I-phase. No appreciable difference in the size and morphology of the first-stage precipitates is seen among the three alloys including the Pt-containing alloy. It is therefore concluded that the first-stage reaction is due to the precipitation of the I-phase with nanograins sizes. The homogeneous formation of the nanoscale 1 structure is attributed to an ease of homogeneous nucleation of the I-phase, followed by the difficulty of grain growth of the I grains. We also examined the X-ray diffraction patterns of the three alloys heated for 3.6 ks at the temperature (1000 K) well above the second exothermic reaction. The diffraction patterns are identified as crystalline Zr₄Al₃, Zr₂Ni and Zr₂Pd phases for M = Pd, Zr₄Al₃, Zr₂Ni and Zr₂Au phases for M = Au and Zr₄Al₃, Zr₂Ni and Zr₂Pt phases for M = Pt. The second exothermic peak is due to the transition from the I-phase to the crystalline mixed phases. It is therefore concluded that the amorphous phase in the Zr₆₅Al₂₅Ni₁₀M₁₇,₅ (M = Pd, Au or Pt) alloys crystallizes through the following processes of amorphous (Am) → Am + I → I → crystalline mixtures of Zr₄Al₃ + Zr₂Ni + Zr₂Pd (Zr₂Au or Zr₂Pt).

4. Discussion

We discuss briefly the reason for the formation of the I-phase at the first stage crystallization of the new Zr–Al–Ni–M (M = Pd, Au or Pt) alloys. It is well known that the Zr–Al–Ni ternary amorphous alloys have a high glass-forming ability leading to the formation of bulk amorphous alloys. The high GFA has been interpreted to result from the unique alloy components which satisfy the three empirical rules for the achievement of high GFA, i.e., (1) multicomponent alloy systems consisting of more than three kinds of elements, (2) significant atomic size mismatch above 12% among the main three elements, and (3) suitable negative heats of mixing among their elements. It has also been confirmed that the Zr–Al–Ni amorphous alloys crystallize through a single exothermic reaction, accompanying with the simultaneous precipitation of crystalline phases of Zr₄Al₃ and Zr₂Ni, and no I-phase is formed. Subsequently, we have reported that the addition of special elements (M = Ag, Pd, Au or
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Pt) leading to the deviation from the three empirical rules for Zr$_{65}$Al$_{17.5}$Ni$_{10}$Cu$_{17.5}$...M$_{x}$ alloys causes the change in the crystallization mode from the single stage to the two stages and the first-stage reaction is due to the precipitation of the I-phase.\(^{6-8}\) As is the case for the Zr–Al–Ni–Cu–M alloys, the M elements with positive heats of mixing against Ni\(^{17}\) are also useful for the formation of the I-phase for the Zr–Al–Ni–M alloys. The high GFA as well as the high stability of the supercooled liquid for the Zr–Al–Ni alloys is due to the formation of a new type liquid structure with highly dense random packed atomic configurations, new local atomic configurations and long-range homogeneous atomic configurations with attractive interactions.\(^{14,15}\) It is presumed that the addition of the M elements with the positive heat of mixing causes a destroy in local regions in the stabilized liquid structure, resulting in the formation of the I-phase as a primary precipitation phase. The clarification on the structure of the Zr–Al–Ni–M amorphous alloys is under investigation and the information will shed light on the detailed mechanism for the effectiveness of the M elements on the formation of the I-phase.

5. Summary

The decomposition behavior of the amorphous alloys including Ni–M atomic pairs with positive heats of mixing was examined in the Zr$_{65}$Al$_{17.5}$Ni$_{10}$M$_{17.5}$ (M = Pd, Au or Pt) systems. It was found that the addition of the M element causes the change in the crystallization mode from single stage to two stages. The first-stage is due to the precipitation of an I-phase and the second stage results from the formation of Zr$_4$Al$_3$ + Zr$_2$Ni + Zr$_2$Pd (Zr$_2$Au or Zr$_2$Pt) phases from the I-phase. The I-phase precipitates from the supercooled liquid and has fine grains with a size of about 10 nm. The nanostructure implies that the nucleation of the I-phase occurs homogeneously and densely while the subsequent growth is sluggish. The formation of the I-phase in the new Zr–Al–Ni–M systems with glass transition is encouraging for the future extension of bulk amorphous and I alloys in the basic science and engineering fields.

REFERENCES