Nanoquasicrystallization in Metallic Glasses

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Nanoquasicrystallization in Zr-based glassy alloys was investigated. It is found that the nano scale icosahedral quasicrystalline phase (I-phase) is formed by addition of the elements, which obstruct the glass-forming ability (GFA) in the glassy alloy. The primary phase of fcc Zr2Ni phase in the Zr65Al15Ni17.5 glassy alloy with high GFA changes to the fcc Zr2Ni plus I-phases by substitution of noble metals or Zr for only 1 at% Cu. Since each phase is precipitated independently and the icosahedral local atomic configuration exits in the fcc Zr2Ni and I-phases, they are originated from the same local structure in the Zr-based glassy alloy with high GFA. We found that the icosahedral local structure is strongly correlated with the stability of the supercooled liquid state. The origin of the icosahedral local structure is combination of Zr + Cu and Zr + Al + Ni elements. In these alloy systems, the I-phase is easy to precipitate as a primary phase by addition of a very small amount of appropriate element. From the present results, it is concluded that the icosahedral local structure stabilizes the supercooled liquid state. We suggest that the high GFA for the preparation of bulk glassy alloy is attributed to the stability of icosahedral local structure.

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Keywords: zirconium-based metallic glass, nano icosahedral phase, transformation, supercooled liquid state, metastable phase, local structure

1. Introduction

Recent discoveries of nanoquasicrystallization of Zr-based glassy alloys with high GFA by addition of 5 to 10 at% elements such as noble metals, V, Nb and Ta1–3 have led us to the clarification of mechanism for the stability of supercooled liquid state in the alloy system, which satisfies three component rules for high GFA.4 It has been reported that the Zr-based glassy alloys have unique local structure in the glassy state, which was completely different from the stable crystalline phases.5,6) These results are also recognized that the stability of supercooled liquid state is strongly correlated with their local structure.5,6) The precipitation of an icosahedral quasicrystalline phase (I-phase) as a primary phase by the slight deviation from highest GFA in the Zr-Al-Ni-Cu alloy system exhibits the possibility of a common structure between the I-phase and local atomic configuration in the glassy state. In this paper, we investigate the stability of the supercooled liquid state in Zr-Al-Ni-Cu glassy alloys by the detailed examination of the transformation behavior. Especially, we have focused on the nanoquasicrystallization in the primary stage, where the precipitation phase reflects the local structure in the glassy or supercooled liquid state. Moreover, the nanoquasicrystallization in the Zr-Al-(Cu or Ni) ternary and Zr-(Cu or Ni) binary systems was investigated. From these studies, we intend to clarify the dominant factor for high GFA and high stability of supercooled liquid state in the Zr-based glassy alloy.

2. Experimental Procedure

Melt-spun Zr-Al-Ni-Cu alloys with a cross section of 0.03 × 1 mm2 were produced from alloy ingots prepared by arc melting high-purity metals of 99.9 mass% Zr, 99.999 mass% Al, 99.9 mass% Ni and 99.999 mass% Cu. Ternary Zr-Al-(Cu or Ni) and binary Zr-(Cu or Ni) alloys were also prepared. The sample preparation was carried out in a purified argon atmosphere. Thermal properties were measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 Ks-1. The samples were annealed in the DSC cell in an argon atmosphere at a heating rate of 1.67 Ks-1. The annealed structure was examined by X-ray diffraction with Cu-Kα radiation and field-emission transmission electron microscopy (FE-TEM) with an accelerating voltage of 300 kV (JEOL JEM-3000F). The sample for TEM observation was prepared by the ion milling technique. The local atomic structure was studied by ordinary X-ray diffraction with monochromatic Mo-Kα radiation from an anticathode operated at 50 kV-200 mA produced by a molybdenum rotary X-ray target and single flat germanium monochromator. The oxygen content of the as-quenched ribbon samples was analyzed to be less than 800 mass ppm by inductively coupled plasma spectroscopy, where the influence of oxygen impurity on the transformation behavior can be disregarded.7

3. Results

3.1 Additional elements for nanoquasicrystallization in the Zr-Al-Ni-Cu glassy alloys

It has been reported that the nano I-phase is precipitated as a primary phase by the addition of appropriate elements of approximately 5 at% in the Zr-based glassy alloy. The additional elements for the I-phase formation in the Zr-Al-Ni-Cu glassy alloy are summarized in Table 1.1–3,8–14) The table contains the atomic radius and mixing enthalpies with Zr, Al, Ni and Cu of the additional elements. It is found that all additional elements have weak or positive mixing enthalpies with one constitutional element at least in Zr-Al-Ni-Cu glassy alloy. Considering the three component rules for high GFA, these results indicate that the slight deviation from high GFA is very effective for the I-phase formation.
The authors have reported the significant increase in the homogeneous nucleation rate by addition of a small amount of Ag or Pd. It is interpreted that the I-phase precipitation leads to the possibility of correlation with the local structure in the glassy state of the Zr-Al-Ni-Cu alloy.

In order to clarify the transition of I-phase precipitation by addition of quasicrystal-forming elements, the initial transformation stage of the Zr\(_{65}\)Al\(_{7}\)Ni\(_{10}\)Cu\(_{16.5}\)Pd\(_{1}\) glassy alloy was examined. Figure 1 shows bright-field TEM images ((a) and (c)) and selected-area electron diffraction patterns (SADP) ((b) and (d)) of the Zr\(_{65}\)Al\(_{7}\)Ni\(_{10}\)Cu\(_{16.5}\)Pd\(_{1}\) glassy alloy annealed for 30 s at 750 K. Two types of particles are observed in Figs. 1(a) and (c). The particles in Fig. 1(a) have a dendrite structure in the diameter range of 200 to 1000 nm in the glassy matrix. The SADP taken from the precipitated particles shown in Fig. 1(b) clearly indicates the quasi-periodic twofold axis, which is identified as an I-phase. In contrast, nearly cuboid particles in the diameter of approximately 500 nm are also observed in the glassy matrix in Fig. 1(c), of which SADP is characterized as the fcc Zr\(_2\)Ni phase along with the [116] zone axis shown in (d). In the Zr\(_{66}\)Al\(_{7}\)Ni\(_{19}\)Cu\(_{17.5}\) glassy alloy, it has been reported that the primary crystalline phase is a metastable fcc Zr\(_2\)Ni with a large lattice parameter of \(a = 1.227\) nm. Therefore, we can

<table>
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<tr>
<th>Additional element</th>
<th>Atomic radius (x10(^{-1}) nm)</th>
<th>Mixing enthalpy (kJ mol(^{-1}))</th>
<th>Reference</th>
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<td>9</td>
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<td>1.47</td>
<td>0 -30 -35 -9</td>
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</table>

Table 1 Additional elements for the I-phase formation in the Zr-Al-Ni-Cu glassy alloy. The atomic sizes and mixing enthalpies with Zr, Al, Ni and Cu are also denoted in the table.
realize that the Zr\textsubscript{65}Al\textsubscript{7}Ni\textsubscript{10}Cu\textsubscript{16.5}Pd\textsubscript{1} glassy alloy transformed from glass to I-phase in addition to the metastable fcc Zr\textsubscript{2}Ni as the primary phases. However, it is found that two phases has a similar Pd content analyzed by nanobeam EDX.\textsuperscript{18) Moreover, these two kinds of precipitates in Figs. 1(a) and (c) are isolated from each other and distributed homogeneously. The precipitation behavior implies the low nucleation rate considering the low distribution density and large grain size at the high annealing temperature near crystallization temperature, $T_x$. Similar precipitation has been confirmed in the Zr\textsubscript{65}Al\textsubscript{7}Ni\textsubscript{10}Cu\textsubscript{16.5} glassy alloys annealed for short time at near $T_x$.\textsuperscript{18) Thus, it is found that the minimum noble metal content for the precipitation of I-phase is 1 at\% in the Zr\textsubscript{65}Al\textsubscript{7}Ni\textsubscript{10}Cu\textsubscript{16.5} glassy alloy. We have reported that the minimum noble metal content for single I-phase formation is approximately 2 at\%\textsuperscript{18})

3.2 Nanoquasicrystallization in the Zr-Al-Ni-Cu glassy alloy without additional elements

The discovery of the I-phase formation in the primary stage by addition of only 1 at\% noble metals suggests us the precipitation of I-phase in the Zr-Al-Ni-Cu glassy alloy by changing the alloy composition from that with the highest GFA. Bright-field TEM images ((a) and (c)) and selected-area electron diffraction patterns (SADPs) ((b) and (d)) of the Zr\textsubscript{66}Al\textsubscript{7.5}Ni\textsubscript{10}Cu\textsubscript{16.5} glassy alloy annealed for 30 s at 735 K. The beam diameter for the selected-area electron diffraction is 1 μm.

Fig. 2 Bright-field TEM images ((a), (c)) and selected-area electron diffraction patterns ((b), (d)) of the Zr\textsubscript{66}Al\textsubscript{7.5}Ni\textsubscript{10}Cu\textsubscript{16.5} glassy alloy annealed for 30 s at 735 K. The beam diameter for the selected-area electron diffraction is 1 μm.

The primary phase changes from the fcc Zr\textsubscript{2}Ni phase to the I-phase by adding a very small amount of noble metals or changing the alloy composition slightly. Since both the phases of fcc Zr\textsubscript{2}Ni and I-phases in the primary stage in these alloys are precipitated in the completely isolated state each other. This result is realized that the fcc Zr\textsubscript{2}Ni and I-phases are originated from the same local structure in the glassy state. Considering that the fcc Zr\textsubscript{2}Ni and I-phases contain an icosahedron as a common local atomic configuration in the unit cell,\textsuperscript{19,20} we can point out that an icosahedral local structure exists in the Zr-Al-Ni-Cu glassy alloy, which can
grow as an icosahedral quasicrystalline phase under high nucleation rate by a small amount of noble metals addition or a slight change in composition. We suggest that a slight difference of symmetry of icosahedral local structure in the glassy state contributes to the phase selection in the primary stage.

Based on the previously reported experimental data for Zr-based glassy alloys, it has been clarified that the glassy alloys can have (a) higher degrees of dense randomly packed atomic configurations, (b) new local atomic configurations, which are different from those of the corresponding final crystalline phases, and (c) homogeneous atomic configurations of the multicomponents on a long-range scale. Assuming the icosahedral local structure, it satisfies the above-described criteria. It is therefore, pointed out that the icosahedral local structure may stabilize the glassy or supercooled liquid state in the Zr-Al-Ni-Cu glassy alloy where the icosahedral order restraints the long-range rearrangements of constitutional atoms to form the ordinary crystalline phases. Finally, it is interpreted that the nano-icosahedral quasicrystallization in Zr-based glassy alloys is attributed to the icosahedral local structure in the glassy state and the enhancement of precipitation due to the increase of nucleation rate.

4. Discussion

4.1 Origin of icosahedral local structure correlated with the stability of supercooled liquid state

It is very important to examine the combination of constitutional elements for the formation of icosahedral local structure. This investigation is useful for searching new glassy alloy with high GFA as well as basic study for the mechanism for high GFA. It is well known that Zr-Al-(Cu or Ni) ternary glassy alloys exhibit the extremely stable supercooled liquid state. We examined the change in the transformation behavior in these alloys by addition of a small amount of Pd. It is the same approach for clarifying the local structure in the Zr-Al-Ni-Cu quaternary alloys. Figure 3 shows XRD patterns of the primary stage in the Zr_{65}Al_{1.5}Cu_{27.5} (a) and Zr_{60}Al_{15}Ni_{25} (b) glassy alloys by addition of 1 to 5 at% Pd substituting for Al and Ni, respectively. In the primary stage, the mixture phases of fcc and Zr_{2}Cu phase are precipitated in the Zr_{60}Al_{15}Ni_{25} glassy alloy. In contrast, the single Zr_{2}Cu phase is formed in the Zr_{65}Al_{7.5}Cu_{27.5} glassy alloy. It was reported that the glassy alloy is transformed through the polymorphous mode from glassy to Zr_{2}Cu phase. By addition of a small amount of Pd, the primary phase changes in both the alloys. The diffraction peak corresponding to I-phase is observed by addition of 3 at% Pd and the single I-phase is confirmed as the primary phase in 5 at% Pd in the Zr_{60}Al_{15}Ni_{25} glassy alloy. Similar tendency is observed in the Zr_{65}Al_{7.5}Cu_{27.5} glassy alloy, where the I-phase formation is confirmed in the 1 at% Pd content. The I-phase precipitation by addition of a small amount element for the deviation from high GFA in the Zr-Al-(Ni or Cu) ternary glassy alloys is recognized as the existence of icosahedral local structure in the glassy or supercooled liquid state.

Similar approach has been applied for the Zr-(Cu or Ni) binary alloys. Figure 4 shows XRD patterns of the primary stage in the melt-spun Zr_{70}Cu_{30} (a) and Zr_{70}Ni_{30} (b) alloys by addition of 0.5 to 1 at% Pd or Au. The obvious change is not confirmed in the Zr_{70}Ni_{30} alloy by addition of Pd or Au in the primary crystallization stage, where the single tetragonal Zr_{2}Ni phase is precipitated. However, the I-phase is formed by addition of a very small amount of Pd or Au in the Zr_{70}Cu_{30} alloy. The minimum Pd or Au content for I-phase formation is approximately 0.5 at%. Bright-field TEM image (a) and NBD pattern (b) of the Zr_{70}Cu_{30}Pd_{1} alloy annealed for 120 s at 620 K are shown in Fig. 5. Very fine particles with a diameter less than 50 nm are observed in the glassy matrix. The NBD pattern in Fig. 5(b) is identified as the I-phase. The nano I-phase formation in the Zr_{70}Cu_{30} alloy by addition of only 0.5 to 1 at% Pd or Au suggests us the existence of the
icosahedral local structure in the glassy state in Zr-Cu alloy. In contrast, it is realized that the different local structure from the icosahedral structure is formed in the Zr$_{70}$Ni$_{30}$ alloy.

4.2 Local structure analysis

The drastic difference in the primary phase by addition of a small amount of noble metals in the Zr$_{70}$(Cu and Ni)$_{30}$ alloys indicates the different local structure between the alloys, leading to the different stability of supercooled liquid state. Figure 6 shows DSC curves of the melt-spun Zr$_{70}$(Cu and Ni)$_{30}$ alloys. The single sharp exothermic reaction is observed after the significant glass transition in the Zr$_{70}$Cu$_{30}$ alloy. The onset temperatures of glass transition, $T_g$ and the exothermic peak, $T_x$ are 627 K and 676 K, respectively. It has been reported that the exothermic peak is clearly separated by addition of 1 at% noble metals such as Pd, Au or Pt with remaining the glass transition. In contrast, a single exothermic peak without glass transition in the melt-spun Zr$_{70}$Ni$_{30}$ alloy. The glass transition cannot be observed even in the 1 at% noble metal-containing Zr-Ni alloys. Comparing the transformation behavior by addition of a small amount of noble metals in the Zr$_{70}$Ni$_{30}$ amorphous and Zr$_{70}$Cu$_{30}$ glassy alloys, we can suggest the correlation between the appearance of the supercooled liquid state before crystallization and the formation of I-phase as a primary phase.

In order to examine the local structure of the melt-spun Zr$_{70}$Cu$_{30}$ and Zr$_{70}$Ni$_{30}$ alloys, a detailed XRD analysis was performed. Radial distribution functions (RDFs) for the melt-spun Zr$_{70}$Cu$_{30}$ (a) and Zr$_{70}$Ni$_{30}$ (b) alloys are shown in Fig. 7. It is seen that the RDFs are completely different in the first peaks. The first peak in the RDF of the Zr$_{70}$Ni$_{30}$ alloy is clearly separated into two peaks which correspond to the
number of the Cu-Cu pair in the melt-spun \( \text{Zr}_{70}\text{Cu}_{30} \) alloy are 0.256 nm and 2.9, respectively, which are different from those (0.322 nm and 4.0) in the tetragonal Zr\(_2\)Cu phase. These results indicate that the local structure in the \( \text{Zr}_{70}\text{Cu}_{30} \) glassy alloy differs from the tetragonal \( \text{Zr}_2\text{Cu} \) structure. Considering that the I-phase is precipitated from the glassy state as a primary phase in the \( \text{Zr}_{70}\text{Cu}_{30} \) glassy alloy by addition of only 0.5 at% Pd or Au, it is suggested that an icosahedral local atomic configuration exists in the glassy state. Since the coordination number around Zr in the glassy state is approximately 12, the icosahedral local atomic configuration may be formed around the Zr atom. The authors have also reported that the icosahedral atomic configuration is confirmed by the high-resolution transmission microscopic observations in the Zr-based glassy alloys, in which the I-phase is formed as a primary phase.\(^{27,28}\)

These results also suggest the investigation of stability of supercooled liquid state in correlation with the local structure. It is well known that high GFA is attributed to a high stability of the supercooled liquid state.\(^{29}\) From the distinct glass transition prior to crystallization in the melt-spun \( \text{Zr}_{70}\text{Cu}_{30} \) alloy, we suggest that the icosahedral local structure stabilizes the supercooled liquid state. We demonstrated that the melt-spun \( \text{Zr}_{70}\text{Ni}_{30} \) alloy which exhibits no distinct glass transition, has the tetragonal \( \text{Zr}_2\text{Ni} \)-like local structure by the RDF analysis. However, it was reported that the glass transition is observed in the rapidly quenched \( \text{Zr}_{70}\text{Ni}_{30} \) alloy.\(^{30}\) Considering the I-phase formation by addition of a small amount of Pd and the total coordination number around Zr of 12.5 in the as-quenched state in the \( \text{Zr}_{60}\text{Ni}_{25}\text{Al}_{15} \) glassy alloy, which is different from those in the crystallized state (13.1) as well as in the melt-spun \( \text{Zr}_{70}\text{Ni}_{30} \) alloy (10.7), we can realize the formation of the icosahedral local structure in Zr-Al-Ni ternary glassy alloy. Therefore, it is concluded that the icosahedral local structure stabilizes the supercooled liquid state and the elemental combinations of Zr + Cu and Zr + Al + Ni are necessary for the icosahedral local structure formation. We also suggest that bulk glass-forming ability is attributed to the difference of stability of the icosahedral local structure with the combination of constitutional elements. The satisfaction of three component rules for high GFA leads to the high stability of icosahedral local structure by retarding the atomic rearrangements for the formation of stable crystalline phase.

5. Conclusions

The mechanism and condition for nanoquasicrystallization in Zr-based glassy alloys are investigated. The nano I-phase is formed by addition of the elements or changing the composition, which obstruct the glass-forming ability (GFA) slightly in the \( \text{Zr}_{65}\text{Al}_{17.5}\text{Ni}_{10}\text{Cu}_{7.5} \) glassy alloy. For example, the minimum content of noble metals for I-phase formation is approximately 1 at%, where the mixture phases of fcc \( \text{Zr}_2\text{Ni} \) and I-phase are independently precipitated as the primary phase. Since the icosahedral local atomic configuration exists in both the phases, it is realized that the icosahedral local structure exists in the glassy or supercooled liquid state in the Zr-Al-Ni-Cu glassy alloy with high GFA. The origin of the components of Zr-Zr and Zr-Ni pairs. These results suggest that the Zr-Ni pair in the \( \text{Zr}_{70}\text{Ni}_{30} \) alloy has strong chemical affinity as compared with the Zr-Cu pair in the \( \text{Zr}_{70}\text{Cu}_{30} \) alloy. All the structural parameters for both the samples in the as-quenched state are summarized in Table 2. Data for crystallized phases, which are calculated from the results in the Ref. 26) are also denoted.

Table 2 Structural parameters for the melt-spun \( \text{Zr}_{70}\text{Cu}_{30} \) and \( \text{Zr}_{70}\text{Ni}_{30} \) alloys. Data for crystallized phases, which are calculated from the results in the Ref. 26).

<table>
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<tr>
<th>Alloys</th>
<th>RDF fitting Parameters</th>
<th>Crystalline phase Parameters</th>
<th>Alloys</th>
<th>RDF fitting Parameters</th>
<th>Crystalline phase Parameters</th>
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<td>( \text{Zr}<em>{70}\text{Cu}</em>{30} )</td>
<td>Zr-Zr 0.322 8.7 Zr 12.4 Tetragonal</td>
<td>Zr-Zr 0.304 4.0 Zr 12.0</td>
<td>( \text{Zr}<em>{70}\text{Ni}</em>{30} )</td>
<td>Zr-Zr 0.315 3.0 Zr 10.7 Tetragonal</td>
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<td>Cu-Cu 0.322 4.0</td>
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Fig. 7 Radial distribution functions (RDFs) for the melt-spun \( \text{Zr}_{70}\text{Cu}_{30} \) (a) and \( \text{Zr}_{70}\text{Ni}_{30} \) (b) alloys.
Icosahedral local structure is in the combination of Zr + Cu and Zr + Al + Ni elements. In these alloy systems, the I-phase is easy to precipitate as a primary phase by addition of a very small amount of appropriate element. Considering that the supercooled liquid region appears in these alloys in DSC curves, it is concluded that the icosahedral local structure stabilizes the supercooled liquid state. We suggest that the high GFA for the preparation of bulk glassy alloy depends on the higher stability of the icosahedral local structure.

REFERENCES