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Precipitations of icosahedral quasicrystalline and crystalline approximant phases in Zr-Al-Ni-Cu-Ir metallic glasses

Chunfei Li*
Inoue Superliquid Glass Project, ERATO, JST, Sendai 982-0807, Japan

Akihisa Inoue
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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Metallic $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ and $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ glasses have been prepared and their crystallization process has been studied with emphasis on the initial stage. The initial precipitation phase is an icosahedral quasicrystalline phase (I phase) for the former alloy and a face-centered cubic Zr_2Ni (fcc-Zr_2Ni) phase for the latter one. Structural analysis revealed that the crystal structure of fcc-Zr_2Ni contains icosahedral atomic clusters, implying that fcc-Zr_2Ni can be regarded as the crystalline approximant for the Zr-based I phase. The preferential precipitation of quasicrystalline/approximant phases in the initial crystallization stage implies the existence of an icosahedral atomic cluster in the glassy states. The compositions of the two alloys were obtained by adding Ir to the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy, which is well known for the formation of a bulk amorphous alloy. The probable existence of icosahedral atomic clusters provided an explanation for the stability of the metallic $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glass.

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Zr-Al-Ni-Cu is an attractive alloy system to researchers engaged in the study of glassy alloys due to its high glass-forming ability,[1,2] which is defined as the necessary cooling rate required to avoid the formation of any detectable crystalline/quasicrystalline phases. Preparation of a bulk amorphous alloy with a diameter up to 16 mm has been successful using the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy.[2] The differential scanning calorimetry (DSC) curve of the as-quenched metallic $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glass shows a large supercooled liquid region ΔT_x, which is defined as the temperature span between the glass transition temperature T_g and the crystallization temperature T_x. The appearance of the large supercooled liquid region at temperatures below T_x is expected to enable the warm working of the bulk glassy alloy to a desired shape. In order to study the reasons for the high stability of the supercooled liquid region, the crystallization process of many Zr-based metallic glasses has been studied. Two significant metastable phases were found in the initial crystallization process, i.e., the fcc-Zr_2Ni (cubic, $Fd3m$ (227), $a = 1.227\,\mathrm{nm}$)[3,4] and I phases. The fcc-Zr_2Ni phase was found in the initial crystallization process of several Zr-Al-Ni-Cu metallic glasses.[5,6] The typical alloy compositions corresponding to the precipitation of the I phase are $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}M_5$ (M = Pd, Pt, Au, and Ag),[7,8] which were obtained via partial substitution of Cu by M in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy. However, it is not clear whether the addition of other elements can cause the formation of an I phase. Furthermore, the role of M metals in the formation of an I phase and the relation of atomic configurations among fcc-Zr_2Ni, the I phase, and the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glassy state remains unclear. In the present work, the non-noble metal Ir was added to the metallic $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glass and its effect on the crystallization process was studied. Depending on the alloy compositions, both the I phase and fcc-Zr_2Ni were found in the initial crystallization process. The relation of local atomic configurations among metallic $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glass, fcc-Zr_2Ni, and the I phase was discussed.

Alloys with nominal atomic percent composition of $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ and $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ were examined. The alloy ingots were prepared by arc melting a mixture of pure metals in an argon atmosphere. From the alloy ingot, a ribbon with a cross section of about $0.03 \times 1\,\mathrm{mm}^2$ was prepared by a single roller melt-spinning method in an argon atmosphere. The melt-spun ribbon was annealed in an evacuated quartz tube. The structure was examined by x-ray diffraction (XRD) and the thermal stability was evaluated by DSC at a heating rate of 0.67 K/s. The microstructure was examined by using a transmission-electron microscope (TEM) JEM-3000F operated at 300 kV. The diameter of the electron beam was focused to 1.0 nm during nanobeam electron diffraction.

Figure 1 shows the DSC curves of the melt-spun ribbons. The metallic glasses change to a supercooled liquid state

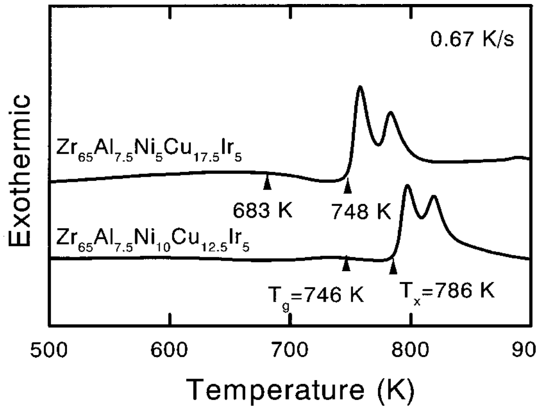

FIG. 1. DSC curves of the melt-spun $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ and $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ ribbons.

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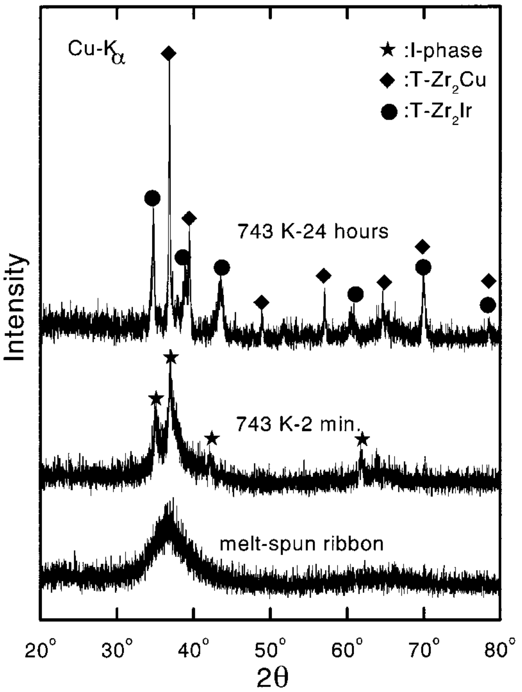

FIG. 2. XRD patterns of the melt-spun and annealed $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ ribbons.

accompanying an endothermic reaction marked with the glass transition temperature T_g, followed by two exothermic peaks. XRD patterns of the $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ alloy are shown in Fig. 2. The halo ring indicates that the melt-spun ribbon is in a glassy state. The diffraction peaks of the ribbon annealed for 2 min at 743 K were identified as an I phase. Further annealing at the same temperature revealed the transformation of the I phase to other regular crystalline phases, indicating that the present I phase is in a metastable state. The XRD patterns of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ ribbons are shown in Fig. 3. The diffraction peaks of the alloy annealed for 3 min at 773 K, which correspond to the low-temperature exothermic reaction, are identified as the fcc-Zr_2Ni phase. Since the phases of the alloy annealed at the same temperature for a longer time are different from fcc-Zr_2Ni, the present fcc-Zr_2Ni phase is also concluded to be in a metastable state. It should be pointed out that the above-indexed results are based on both the XRD analysis and the TEM observation to be presented later.

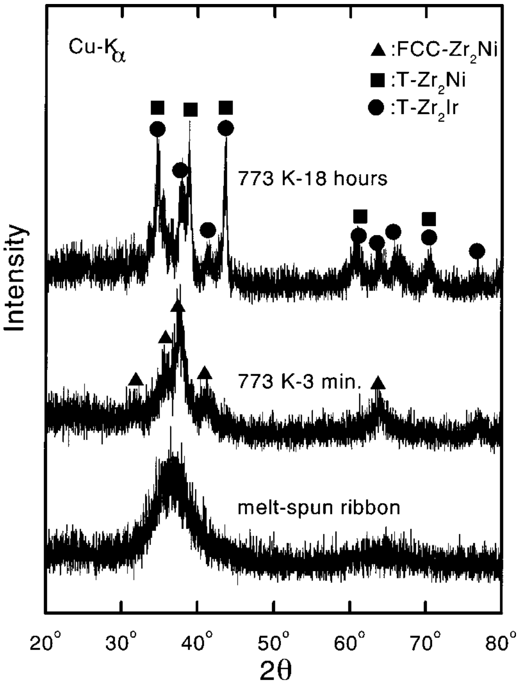

FIG. 3. XRD patterns of the melt-spun and annealed $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ ribbons.

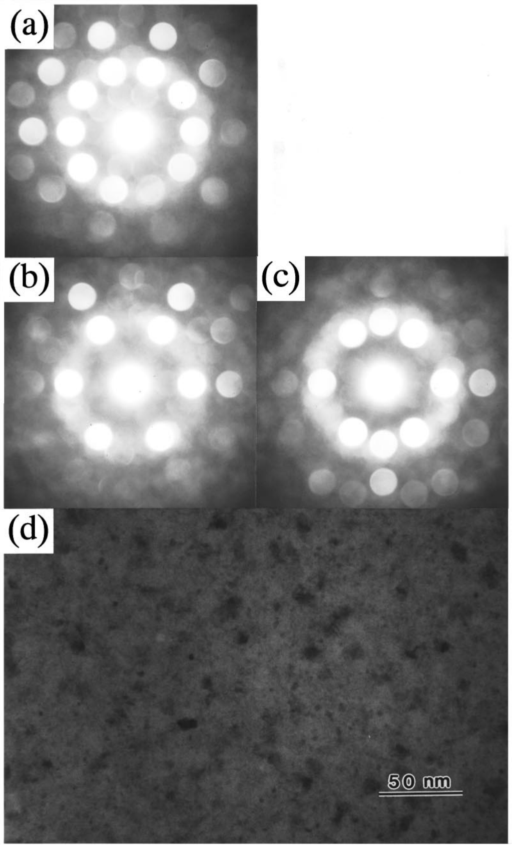

FIG. 4. Results of TEM observation of the $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ alloy annealed for 2 min at 743 K. (a), (b), and (c) show the nanobeam electron-diffraction patterns, corresponding to the five-, three-, and twofold symmetries of the I phase, respectively. The bright-field TEM image shown in (d) indicates that the size of the precipitated particles is approximately 13 nm.

Figure 4 shows the results of TEM observation of the $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ ribbon annealed for 2 min at 743 K. (a), (b), and (c) are nanobeam electron-diffraction patterns corresponding to the five-, three-, and twofold symmetries, respectively. From these diffraction patterns, it has been firmly established that the initial precipitation phase is an I phase. The bright-field TEM image shown in (d) indicates that the precipitated particle size is approximately 13 nm. The results of TEM observation of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ ribbon annealed for 3 min at 773 K are shown in Fig. 5. Figure 5(a) is the observed nanobeam electron-diffraction pattern from the

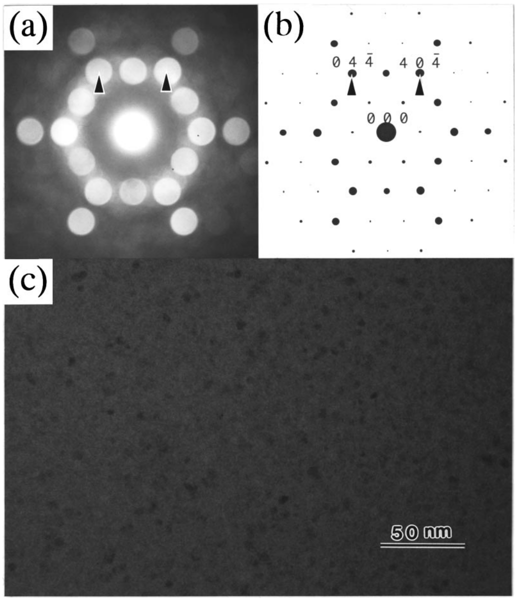

FIG. 5. Results of TEM observation of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ alloy annealed for 3 min at 773 K. The nanobeam electron-diffraction pattern (a) is in agreement with the simulated one (b), which was obtained based on the crystal structure of fcc-Zr_2Ni. The bright-field TEM image shown in (c) indicates that the size of the precipitated particles is approximately 7 nm.

precipitated particle. Figure 5(b) is the simulated one based on the crystal structure of fcc-Zr_2Ni, where the incident electron beam is parallel to the $\langle 111 \rangle$ orientation. Spots in Fig. 5(b) with high intensity are in agreement with those in Fig. 5(a), implying that the precipitated particle has the fcc-Zr_2Ni structure. The bright-field TEM image shown in Fig. 5(c) indicates that the particle size is approximately 7 nm.

The fcc-Zr_2Ni appears to be a crystalline approximant of the Zr-based I phase. As shown in Figs. 5(a) and 4(b), the electron-diffraction pattern of fcc-Zr_2Ni taken with the incident electron beam parallel to the $\langle 111 \rangle$ crystalline orientation resembles the threefold symmetry diffraction pattern of the I phase. This reminds us of the possible structural similarity between fcc-Zr_2Ni and the I phase. In the previous report, the structure of fcc-Zr_2Ni has been described as consisting of a tetrahedron formed by Ni atoms and an octahedron formed by Zr atoms.[3,4] These polyhedrons are shown in the upper part of Fig. 6. From the above-mentioned experimental results, we analyzed the crystal structure from the point of view of an icosahedral atomic cluster. It was found that the atoms between the Ni tetrahedron and the Zr octahedron form an icosahedron. This portion is enlarged in the lower part of Fig. 6. One vertex of the Ni tetrahedron occupies the center site of the icosahedron. The Ni atom is surrounded by nine Zr and three Ni atoms, forming an $Ni(Zr,Ni)_{12}$ icosahedral atomic cluster. It should be pointed out that this icosahedron is distorted. On the shell of the icosahedron, the Ni-Ni interatomic distance is smaller than that of Zr-Zr, implying that distortion of the icosahedron is mainly caused by the difference in atomic radius between Zr and Ni.

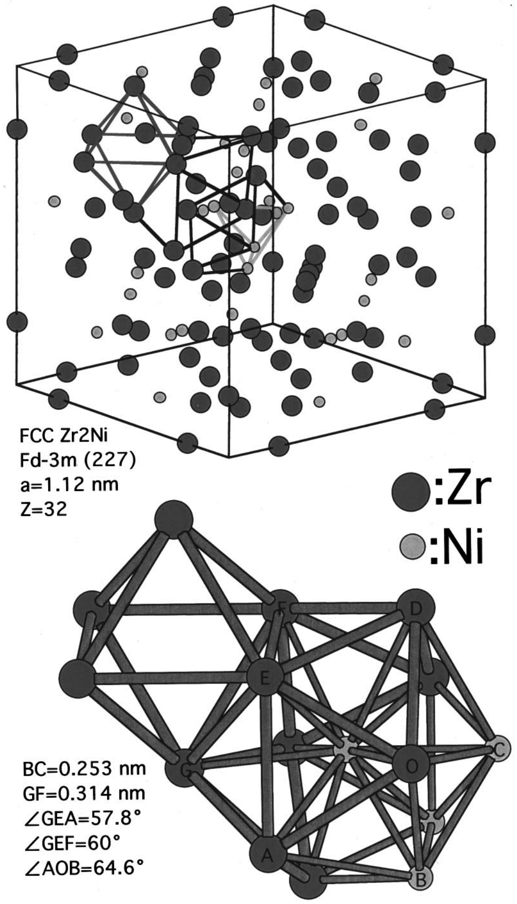

FIG. 6. Schematic drawing of the fcc-Zr_2Ni crystal structure. The upper part is the unit-cell view. The enlarged portion shown in the lower part illustrates the relationship among the Ni tetrahedron, Zr octahedron, and icosahedron.

Therefore, the initial precipitation phase in the present Zr-Al-Ni-Cu-Ir alloys is characterized by the possession of icosahedral atomic clusters in their local atomic configurations. This suggests icosahedral atomic clusters exist in the glassy alloys with compositions around $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$. The existence of such icosahedral atomic clusters in the metallic glass provides the seeds for the precipitation of both an I phase and fcc-Zr_2Ni. The precipitation of an fcc-Zr_2Ni phase in the metallic $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ glass is due to its compositional similarity to fcc-Zr_2Ni. Stable Ti_2Ni and Hf_2Ir crystalline phases with the same structure as fcc-Zr_2Ni were reported.[9] However, such phases were not reported in alloys containing Cu and Al. Therefore, it is assumed that Ni and Ir are suitable to the Ni site in the fcc-Zr_2Ni crystal, and Al and Cu are not suitable. The Zr atomic concentration in the present alloys remains as 65 at. %, which is approximately the same as that required from the chemical formulas of fcc-Zr_2Ni. The Ni sites in the fcc-Zr_2Ni crystalline phase should be occupied by Ni, Cu, Al, and Ir atoms. For the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ alloy, the atomic percent of elements suitable to the Ni site is 15 at. %, which is higher than that in $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ (10 at. %) and $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ (10 at. %). This explains why the metastable fcc-Zr_2Ni phase was found in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ and was not found in the other two alloys. On the other hand, the atomic concentration of elements suitable to the Ni site is 10 at. % for the $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ alloy, which may be too low for the precipitation of an fcc-Zr_2Ni-type crystalline phase. Further, the atomic radius of Ir (0.135 nm) is larger than that of Ni (0.125 nm).[10] This makes the Ni tetrahedron distorted and the icosahedral atomic cluster less distorted. As a result, the I phase precipitates in the initial crystallization process. Noticing the atomic radii of Ir (0.135), Pd (0.137), Au (0.144), and Ag (0.144 nm),[10] the above discussion based on the atomic size effect should apply to the I-phase precipitation in metallic $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}M_5$ ($M=$Pd, Pt, Au, and Ag) glasses, which has been reported previously. With respect to the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy, the precipitation of fcc-Zr_2Ni is retarded because of the low concentration of elements suitable to the Ni site. The precipitation of the I phase is retarded because of the lack of elements, making the icosahedral atomic cluster less distorted. The glassy state translates directly to the stable crystalline phases.[11] The precipitation of these stable crystalline phases from the glassy matrix requires the elemental redistribution across the icosahedral atomic cluster, which is difficult. The low atomic mobility in the metallic glass contributes to the high thermal stability of the supercooled liquid.

In summary, the initial precipitation phases are the I phase and fcc-Zr_2Ni for the $Zr_{65}Al_{7.5}Ni_5Cu_{17.5}Ir_5$ and $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ir_5$ metallic glasses, respectively. Ir is verified to be effective in promoting the formation of a Zr-based I phase, adding to the previously reported noble metals. Structural analysis revealed that fcc-Zr_2Ni serves as the crystalline approximant for the Zr-based I phase. Preferential precipitation of the I phase and its crystalline approximant leads to the speculation that icosahedral atomic clusters exist in the glassy alloys in the vicinity of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$. This suggestion provides an explanation to the high thermal stability of the supercooled liquid state of metallic $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glass.

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*Corresponding author. FAX: 022-243-7616. Email address: li@sendai.jst.go.jp

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