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Primary precipitation of icosahedral quasicrystal with rearrangement of constitutional elements in $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy with low oxygen impurity

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The primary transformation reaction of the $Zr_{65}Al_{7.5}Cu_{27.5}$ ternary glassy alloy with a low oxygen impurity of approximately 100 mass ppm was investigated. We have discovered the precipitation of the metastable icosahedral phase with a fine grain size of 50–100 nm in diameter accompanying with the formation of stable Zr_2Cu phase at the annealing temperatures ranging from 715 to 730 K. The lattice spacing of Zr_2Cu phase decreases at higher temperatures, which is attributed to the rearrangement of Zr and Cu in the decomposition of the icosahedral phase. It is suggested that the formation of the icosahedral phase in the primary stage originates from the existence of the quenched-in icosahedral local atomic configuration in the glassy state.

A number of glassy alloys with high glass-forming ability (GFA) have been reported and have attracted much attention in the aspects of the application of bulky shape as well as the fundamental investigation of the mechanism of high stability of supercooled liquid state.[1,2] Among the bulk glassy alloys, Zr–Al–TM (TM stands for transition metal) alloys are particularly interesting due to their high GFA.[3] Recently, since the formation of nano icosahedral quasicrystalline phase as a primary precipitation phase in various Zr-based glassy alloys was reported,[4–6] great attention has also been focused on investigating the mechanism in the viewpoint of the structural correlation between high GFA and icosahedral local atomic configurations.[7–9] However, the addition of small amount of elements such as noble metals or oxygen impurity, where these elements obstruct the high GFA, is necessary for the formation of icosahedral phase in the previous Zr-based alloys.[6,10–12]

A $Zr_{65}Al_{7.5}Cu_{27.5}$ ternary glassy alloy is recognized as the alloy composition exhibiting the extremely wide supercooled liquid region approximately 90 K, defined as the temperature interval between glass transition temperature and crystallization temperature.[13] It is reported that the transformation process is drastically changed from the single reaction into two-stage reaction by oxygen content, where the first reaction corresponds to a formation of icosahedral quasicrystalline phase.[12] The oxygen-induced primary quasicrsytallization is observed in the oxygen content above 0.43 at.% (900 mass ppm).[14] It is also reported that the polymorphous crystallization from the glassy to Zr_2Cu phase takes place at the oxygen content of 0.14 at.% (300 mass ppm). However, detailed examination in the initial crystallization process was not carried out for the alloy with low oxygen content in the previous studies. In this paper, we report the formation of icosahedral phase together with the Zr_2Cu phase and the rearrangement behavior of constitutional elements in the primary transformation stage in the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy with oxygen content below 100 mass ppm. It is recognized as the first observation of icosahedral phase formation without additional elements and significant rearrangement behavior during transformation in the alloy.

Melt-spun $Zr_{65}Al_{7.5}Cu_{27.5}$ ternary alloy ribbon with a cross section of 0.03×1 mm^2 was produced from alloy ingot prepared by arc melting high purity metals of 99.9 mass% crystal Zr, 99.999 mass% Al, and 99.999 mass% Cu in a purified argon atmosphere. The raw material of crystal Zr contains the impurities of 0.038 mass% Hf, 0.013 mass% Fe, and other elements such as Cr, Nb, Ni, Ta, and Ti etc. with the concentrations less than 0.005 mass%. We have also detected the oxygen concentration less than 10 mass ppm by chemical analysis. The holding time in the melted state of the alloy in the quartz tube was shortened comparing to those in our previous works to prevent from the reaction between the melt and quartz tube. The purity of Ar gas was also much higher than that in the previous ones. The structure

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and thermal stability of the as-spun ribbon were measured by x-ray diffraction (XRD) analysis with Cu K_α radiation with 40 kV to 40 mA and differential scanning calorimetry (DSC) with heating rate of 0.67 K/s. The sample was annealed in a purified Ar atmosphere at a heating rate of 1.67 K/s. The structure of annealed samples was examined by XRD and field-emission transmission electron microscopy (FE-TEM) with an accelerating voltage of 300 kV (JEOL JEM-3000F; Tokyo, Japan). The micro structure was analyzed by nano beam electron diffraction with a beam diameter of 2.4 nm. The composition was measured by the nano beam energy dispersive x-ray (EDX) spectroscopy. Sample preparation for TEM observation was used by the ion milling technique.

The oxygen content of the melt-spun $Zr_{65}Al_{7.5}Cu_{27.5}$ ribbon is approximately 100 mass ppm analyzed by inductively coupled plasma spectroscopy, where the influence of oxygen impurity on the transformation behavior can be ignored.[12] The single exothermic peak after the significant glass transition is exhibited in the DSC curve. The temperatures of glass transition T_g, crystallization T_x, and the exothermic peak T_p are 642, 736, and 756 K, respectively. These temperatures are consistent with those in the previous studies.[13] The XRD patterns of the samples annealed for 120 s at temperatures ranging from 715 to 735 K are shown in Fig. 1. Data for as-quenched state are also denoted in Fig. 1. Only the halo pattern is observed at the as-quenched state and all the peaks can be corresponding to the Zr_2Cu phase at 735 K. In the temperature range of 715–730 K, the extra peaks are confirmed in addition to the peaks of Zr_2Cu phase. The peaks appear at the approximately $2\theta = 35.1°$, 42.3°, and 61.2°. Moreover, the sub peak with $2\theta = 37.0°$ is confirmed within the main peak of the Zr_2Cu phase around $2\theta = 36.7°$. Among them, the peak of $2\theta = 35.1°$ is indicated by arrows in Fig. 1. Due to the sudden disappearance of these peaks with an increase of the annealing temperature or increase of the annealing time (not shown here), it is suggested the metastable phase formation in the initial stage. We found that these peaks are corresponding to those of the primary precipitated icosahedral phase in the Zr-based metallic glasses such as $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ alloy.[10]

To examine the structure of metastable phase, we performed transmission electron microscopic observation for the annealed glassy alloy. Figure 2 shows the (a) bright-field (BF) TEM image, (b) selected-area electron diffraction pattern (SADP), and (c–e) nano beam electron diffraction (NBD) patterns with a beam diameter of 2.4 nm of the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy annealed for 120 s at 725 K. In the BF image, two kinds of particles with coarse dendritic and fine spherical morphologies are observed. The coarse particle has a diameter over 500 nm. The SADP pattern taken from the coarse particle shown in Fig. 2(b) is characterized as the Zr_2Cu phase. In contrast, the size of fine particles is in the diameter of 50 to 100 nm and they are precipitated homogeneously. The NBD patterns taken from the fine particles reveal the quasiperiodic 5-, 3-, and 2-fold symmetries as shown in Figs. 2(c)–2(e). Therefore, it is concluded that the

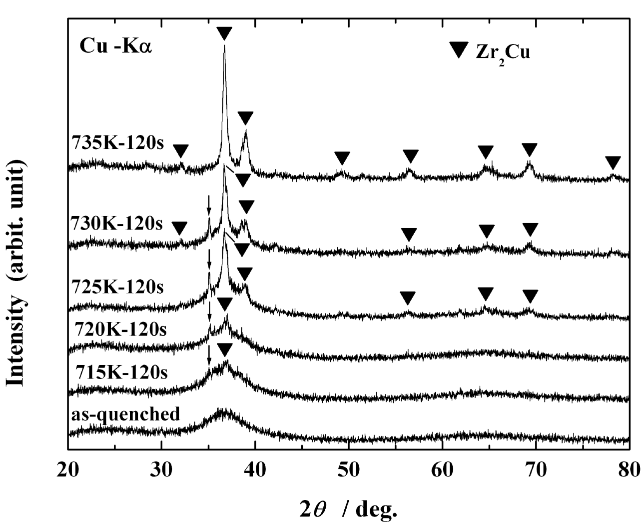

FIG. 1. XRD patterns of the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy annealed for 120 s at the temperature range of 715–735 K. Data for as-quenched state is also denoted.

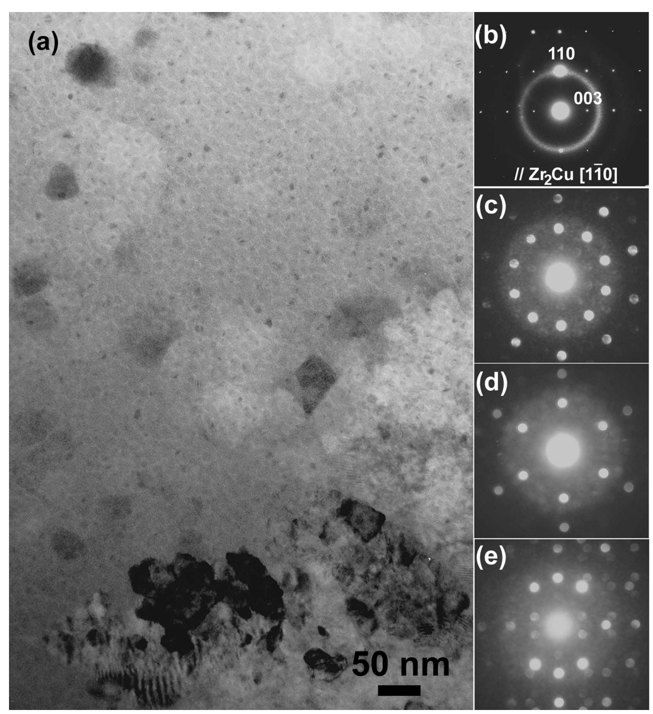

FIG. 2. (a) Bright-field (BF) TEM image, (b) selected-area electron diffraction pattern (SADP), and (c–e) nano beam electron diffraction (NBD) patterns with a beam diameter of 2.4 nm of the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy annealed for 120 s at 725 K.

icosahedral quasicrystalline and Zr_2Cu phases are simultaneously formed in the initial crystallization stage of the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy. Figure 3 shows the high-resolution transmission electron microscopy image of the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy annealed for 120 s at 725 K. The icosahedral and Zr_2Cu phases are characterized by their electron-diffraction patterns, which are denoted in the figure as QC and Zr_2Cu, respectively. The icosahedral phase is precipitated homogeneously with independent of the Zr_2Cu phase. Moreover, we found that the glassy phase remains with these two phases in the annealing condition. It is speculated that the homogeneous distribution with fine grain size of the icosahedral particles originates from the icosahedral local atomic configuration in the glassy state.[7,15] Considering the change in XRD patterns with annealing temperature, the icosahedral phase decomposes at the temperatures higher than 730 K.

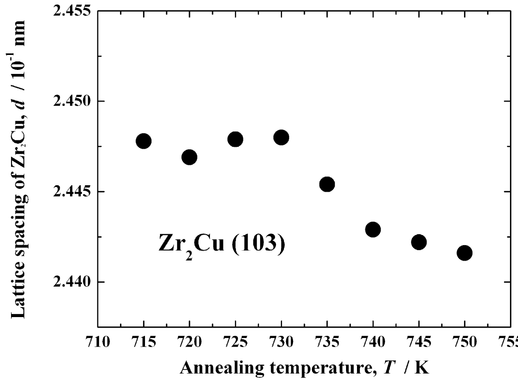

FIG. 4. Change in the lattice spacing, d of Zr_2Cu (103) with annealing temperature in the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy. The annealing time is fixed for 120 s. The lattice spacing, d is calculated from XRD patterns measured at room temperature.

Table I summarizes the composition of icosahedral, Zr_2Cu and residual glassy phases in the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy annealed for 120 s at 725 K. The average compositions of five data points in the icosahedral, Zr_2Cu, and residual glassy phases are $Zr_{74.5}Al_{4.8}Cu_{20.7}$, $Zr_{71.5}Al_{5.3}Cu_{23.2}$, and $Zr_{68.9}Al_{5.6}Cu_{25.5}$, respectively, which reveals that Zr is enriched in and Cu and Al are rejected from the icosahedral phase. In contrast, the Zr_2Cu phase at the initial state has a rich Zr and poor Cu contents. The Al content in the Zr_2Cu phase seems to be similar to that in the glassy phase. These results indicate that a significant rearrangement is required for the transformation in the initial stage in the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy. Figure 4 shows the change in the lattice spacing, d of Zr_2Cu (103) with annealed temperature in the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy. The annealing time is fixed for 120 s. The lattice spacing is calculated from the XRD peaks measured at room temperature. The icosahedral and Zr_2Cu phases are formed at the temperatures below 735 K. At the primary state with coexistence of icosahedral and Zr_2Cu phases, the lattice spacing of Zr_2Cu (103) is approximately 2.448×10^{-1} nm. With disappearance of the icosahedral phase as well as glassy phase, the lattice spacing decreases to 2.442×10^{-1} nm at 750 K. We found that the lattice spacing decreases slightly at higher annealing temperatures and is getting to be 2.440×10^{-1} nm at 873 K. Similar tendency of a decrease in lattice spacing is observed in other planes. We can estimate the lattice constant of Zr_2Cu phase as $a = 3.262 \times 10^{-1}$ nm, $c = 11.11 \times 10^{-1}$ nm for the annealing temperatures below 735 K and $a = 3.254 \times 10^{-1}$ nm, $c = 11.08 \times 10^{-1}$ nm for the annealing temperatures above 735 K. Considering the composition difference among the phases in the initial stage as shown in Table I, it is suggested that the Zr content decreases and Cu content increases in the Zr_2Cu phase in the final stage. Since the atomic radii of Zr and Cu are 1.62 and 1.28×10^{-1} nm, respectively, it is realized that the decrease of lattice spacing of Zr_2Cu phase is attributed to the compositional change with a proceeding of the transformation reaction. Concerning the influence of rearrangement of Al, it is not possible to detect the significant composition difference between the Zr_2Cu and glassy phases by EDX due to the light metals with a low concentration. However, we suggest that the rearrangement of Al also plays an important role for the transformation due to the composition difference between the icosahedral and Zr_2Cu phases. These studies are recognized as the first investigation that shows the icosahedral quasicrystalline phase is formed in the initial stage and the significant rearrangement of constitutional elements takes place through the transformation reaction in the $Zr_{65}Al_{7.5}Cu_{27.5}$ ternary glassy alloy containing

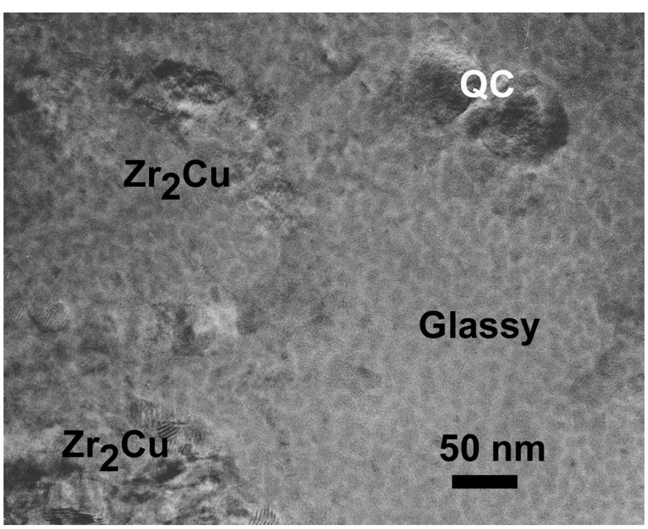

FIG. 3. High-resolution transmission electron micrograph of the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy annealed for 120 s at 725 K.

TABLE I. EDX results for the precipitated phases and residual glassy phase in the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy annealed for 120 s at 725 K.

		Zr	Al	Cu	(at.%)
Icosahedral		74.9	4.5	20.6	
		74.5	4.5	21.0	
		74.9	4.9	20.2	
		75.0	5.3	19.7	
		73.4	4.7	21.9	
	Average	74.5	4.8	20.7	
Zr_2Cu		72.2	5.3	22.5	
		71.6	4.9	23.5	
		70.7	5.5	23.8	
		72.0	5.4	22.6	
		70.7	5.5	23.8	
	Average	71.5	5.3	23.2	
Glassy		69.2	5.0	25.8	
		69.2	5.0	25.8	
		69.2	5.9	24.9	
		67.9	6.2	25.9	
		69.3	5.7	25.0	
	Average	68.9	5.6	25.5	

low oxygen impurity. Based on the present study, the transformation process is summarized as follows

$$\begin{aligned}\text{Glassy phase} &\rightarrow \text{icosahedral (Zr-rich, Al- and Cu-poor)}\\ &+ Zr_2Cu \text{ (Zr-rich, Cu-poor)}\\ &+ \text{glassy phase (Zr-poor, Cu-rich)}\\ &\rightarrow Zr_2Cu \quad .\end{aligned}$$

In conclusion, the initial transformation reaction in the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy was investigated in detail. We found the primary precipitation of the icosahedral quasicrystalline phase in addition to the Zr_2Cu phase. The size of icosahedral particles is very fine with diameter of 50–100 nm and distributed homogeneously, which is speculated that the existence of icosahedral local atomic configuration in the glassy state. The significant compositional difference among the icosahedral, Zr_2Cu and residual glassy phases is detected. With decomposition of the icosahedral phase, the lattice spacing of the Zr_2Cu phase decreases. It is attributed to the rearrangement of constitutional elements especially Zr and Cu. Finally, we suggest that the necessity of rearrangement of constitutional elements during the transformation is strongly correlated with the stability of supercooled liquid state and/or high GFA of the $Zr_{65}Al_{7.5}Cu_{27.5}$ glassy alloy.

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