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Direct observation of icosahedral cluster in $Zr_{70}Pd_{30}$ binary glassy alloy

Junji Saida[a] and Mitsuhide Matsushita
Inoue Superliquid Glass Project, ERATO, Japan Science and Technology Corporation (JST), Yagiyamaminami 2-1-1, Sendai 982-0807, Japan

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

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The medium-range order in the $Zr_{70}Pd_{30}$ binary glassy alloy, where the nanoicosahedral phase precipitates as a primary phase, was examined using the high-resolution electron microscopic technique. The ordered region in the diameter of ~2 nm was observed in the as-quenched glassy state. This region grows slightly to the diameter of 3–4 nm by annealing for 120 s at 690 K, where the amorphous structure remains. The nanobeam electron diffraction pattern taken from the medium-range order shows the fivefold symmetry, indicating that this region has the icosahedral structure. This result is recognized as a direct evidence for the existence of the icosahedral cluster in the alloy. For further annealing for 600 s at 690 K, the icosahedral quasicrystalline phase in the diameter of 5–8 nm precipitates by assimilating the icosahedral cluster. The formation of the nanoicosahedral phase originates from the existence of the quenched-in icosahedral clusters in the glassy state followed by their easy growth to the icosahedral particle without significant rearrangement of the constitutional elements.
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Since the reproducible formation of a nanoicosahedral quasicrystalline phase as a primary precipitation phase in the Zr–Al–Ni–Cu–NM,[1,2] Zr–Al–Ni–NM,[3] (NM=Ag, Pd, Au, Pt), and Zr–TM–M,[4,5] (TM=Fe, Ni, Co, Cu, M=Pd, Au, Pt) glassy alloys was reported, great attention has been focused on investigating the reason for the formation of the icosahedral phase in the Zr-based glassy alloys in the aspects of the structural correlation[6] between high glass-forming ability and icosahedral atomic configurations. In prior studies,[6] it was revealed that ordered regions exist in the glassy state in the $Zr_{54.5}Ti_{7.5}Cu_{20}Ni_8Al_{10}$ multicomponent alloy. However, the ordered regions were too small to identify their structure. More recently, the authors have confirmed the nanoicosahedral phase as a primary phase transformed from the glassy state in the $Zr_{70}Pd_{30}$ binary alloy.[7] In this letter, we have examined the existence and structure of the medium-range order in the as-quenched and annealed $Zr_{70}Pd_{30}$ binary glassy alloy using the high-resolution electron microscopic and nanobeam electron diffraction techniques.

Melt-spun $Zr_{70}Pd_{30}$ ribbon sample with a cross section of $0.03\times 1\ \mathrm{mm}^2$ was produced from alloy ingot prepared by arc melting high purity metals of 99.9 mass % crystal Zr and 99.9 mass % Pd in a purified argon atmosphere. The medium-range ordering was examined by field-emission transmission electron microscopy (FETEM) with an accelerating voltage of 300 kV (JEOL JEM-3000F). The structure of the medium-range order was analyzed by nanobeam electron diffraction with a beam diameter of 1 nm. Sample preparation for TEM observation was used by the ion milling technique. Isothermal annealing was performed in a differential scanning calorimetry (DSC) equipment at 690 K (just below the glass transition temperature) for 120 and 600 s. Heating to the isothermal temperature was performed at a high rate of $1.67\ \mathrm{K\,s^{-1}}$ to suppress thermal influences during heating. The compositions of the icosahedral and residual glassy phases were examined by energy dispersive x-ray (EDX) spectroscopy with a beam diameter of 2.4 nm.

The oxygen content of the melt-spun $Zr_{70}Pd_{30}$ ribbon is below 700 mass % ppm analyzed by inductively coupled plasma spectroscopy, where the influence of oxygen impurity on the transformation behavior can be ignored.[8] It has already been reported that the crystallization proceeds through two exothermic reactions after glass transition in the $Zr_{70}Pd_{30}$ glassy alloy.[7] The onset temperatures of glass transition, T_g and the first exothermic peak are 701 and 723 K, respectively, where the temperatures are measured by DSC at a heating rate of $0.67\ \mathrm{K\,s^{-1}}$. The temperature interval between the two exothermic peaks is ~80 K. From the transformation behavior of the two exothermic reactions, it is found that the first peak is due to the precipitation of the icosahedral phase with nanometer scale from the glassy phase and the second peak results from the transformation from the icosahedral phase to the Zr_2Pd phase.[7]

In order to examine the medium-range order, we performed high-resolution transmission electron microscopic observation for the as-quenched glassy alloy. Figure 1 shows the high-resolution TEM image (a) and selected-area electron diffraction pattern (SADP) taken from the region of 1 μm diameter (b) of the as-quenched $Zr_{70}Pd_{30}$ glassy alloy. The SADP consists of the halo ring and no diffraction spots can be observed, indicating that the melt-spun sample has a glassy structure. In Fig. 1(a), it is found that the image has some features of local ordered regions which are circled in

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[a] Electronic mail: jsaida@sendai.jst.go.jp

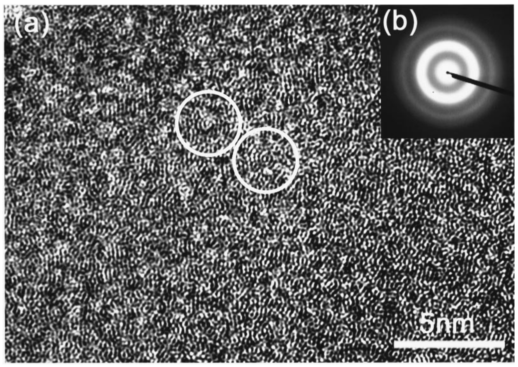

FIG. 1. High-resolution transmission electron micrograph (a) and selected-area electron diffraction (b) of the melt-spun $Zr_{70}Pd_{30}$ glassy alloy. The beam diameter for the selected-area electron diffraction is 1 μm.

the figure. The size of the ordered regions is $\sim$2 nm in diameter. We could not obtain any nanobeam diffraction patterns except a halo ring from the ordered region owing to the extremely small size. However, a similar ordered contrast has been reported in the simulation results where the icosahedral medium-range order is assumed to exist in the amorphous state.[9] Moreover, Xing *et al.* have recently reported the similar structure in the as-quenched $Zr_{54.5}Ti_{7.5}Cu_{20}Ni_8Al_{10}$ glassy alloy,[6] where the icosahedral phase is also formed in the annealed state. They suggest that the ordered contrast is indicative of an icosahedral cluster. It may therefore be thought that the ordered region observed in the as-quenched $Zr_{70}Pd_{30}$ glassy alloy is realized as an icosahedral cluster.

For further structural identification, TEM observation was performed in the low temperature annealed sample. Figure 2 shows the high-resolution TEM image (a), SADP taken from the region of 1 μm diameter (b) and nanobeam electron diffraction (NBD) pattern with a beam diameter of 1 nm (c) of the $Zr_{70}Pd_{30}$ glassy alloy annealed for 120 s at 690 K. The annealing temperature is just below the glass transition temperature and the glassy structure remains in this condition as shown in Fig. 2(b). Moreover, neither precipitation of a crystalline nor a quasicrystalline phase can be seen in the high-resolution image. It is confirmed that the same ordered region as that in the as-quenched sample is observed in the high-resolution image, as marked with a circle in Fig. 2(a). The size of the ordered region increases slightly to the diameter range of 3–4 nm as compared with that in as-quenched sample. The NBD pattern taken from the ordered region (marked A in the high-resolution image) is shown in Fig. 2(c). Although the diffraction spots are significantly weak due to the small area of the ordered region and a fine electron beam, the fivefold symmetry is clearly identified, which indicates that the cluster has the icosahedral structure. These results are regarded as the first evidence for the structural identification of the icosahedral cluster of the $Zr_{70}Pd_{30}$ glassy alloy, implying that the icosahedral cluster observed in the as-quenched state is attributed to the high stability of the icosahedral atomic configuration during the cooling process from the melt. The stable icosahedral cluster is presumed to originate from the strong chemical affinity between Zr and Pd, which leads to the restraint of the rearrangements of constitutional elements to form the periodic crystalline phase.

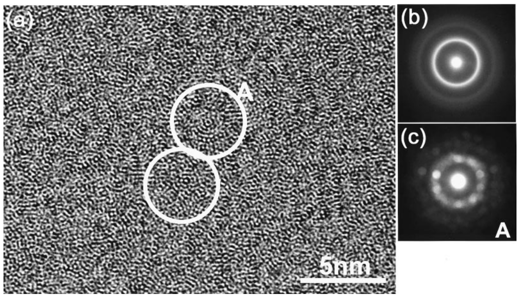

FIG. 2. High-resolution transmission electron micrograph (a), selected-area electron diffraction (b), and nanobeam electron diffraction pattern (c) of the $Zr_{70}Pd_{30}$ glassy alloy annealed for 120 s at 690 K. The beam diameters for the selected-area electron diffraction and nanobeam electron diffraction are 1 μm and 1 nm, respectively.

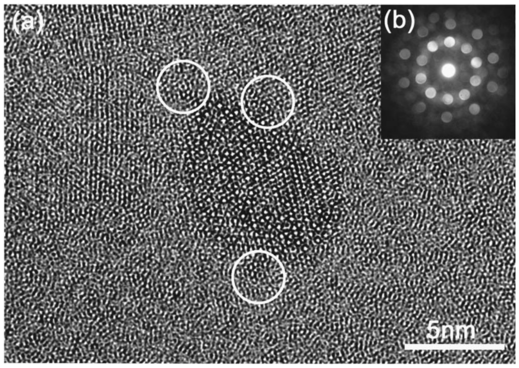

FIG. 3. High-resolution transmission electron micrograph (a) and nanobeam electron diffraction (b) of the $Zr_{70}Pd_{30}$ glassy alloy annealed for 600 s at 690 K. The beam diameter for the nanobeam electron diffraction is 1 nm.

For the investigation of the growth process of the icosahedral cluster, we annealed the sample for longer time at 690 K. The high-resolution image of the $Zr_{70}Pd_{30}$ glassy alloy annealed for 600 s at 690 K is shown in Fig. 3(a). Several precipitates in the diameter range of 5–8 nm are observed. Since the NBD pattern taken from the precipitate in the center of the high-resolution image clearly indicates the fivefold symmetry as shown in Fig. 3(b), these precipitates are identified as an icosahedral quasicrystalline phase. It is suggested that the quasicrystallization proceeds by the rearrangement of atoms due to the long annealing time at the temperature below T_g. The icosahedral cluster is detected simultaneously around the interface between the icosahedral particle and glassy phase, which are circled in the image. This result implies that the icosahedral cluster can grow easily to the icosahedral quasicrystalline particles with assimilating the clusters. The authors have also reported that the transformation from glassy to icosahedral phase proceeds through the diffusion-controlled process with compositional change.[10] However, the average composition of five data points in the icosahedral phase obtained by EDX spectroscopy is $Zr_{74.1}Pd_{25.9}$, which is relatively close to that ($Zr_{70.9}Pd_{29.1}$) in the residual glassy phase. It is, therefore suggested that the growth of the icosahedral cluster to icosahedral quasicrystalline phase takes place by the slight rejection of Pd.

The medium-range ordering in the melt-spun $Zr_{70}Pd_{30}$ glassy alloy is observed in the high-resolution image using FETEM. The size of the ordered region is $\sim$2 nm in diameter, where the image is quite similar to that of the simulation results where the icosahedral medium-range order is assumed to exist in the glassy state. The ordered region grows slightly to 3–4 nm diameter in the annealed state for 120 s at 690 K. Since the NBD pattern taken from the ordered region indicates the fivefold symmetry, the ordered region is recognized as the icosahedral cluster. It is pointed out that this result is the direct evidence for the existence of icosahedral clusters in the melt-spun $Zr_{70}Pd_{30}$ glassy alloy. In the sample annealed for 600 s at 690 K, the icosahedral particles in the diameter range of 5–8 nm precipitate and the icosahedral clusters are also observed around the interface between the icosahedral particle and glassy phase. From the compositional analyses between the icosahedral and residual glassy phases, it is realized that the icosahedral cluster can grow to the icosahedral phase by a slight rejection ($\sim$3 at. %) of Pd element. In conclusion, the existence of the stable icosahedral cluster followed by its easy growth to the icosahedral particle are the dominant factors for the formation of nanoicosahedral quasicrystalline phase in this alloy.

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