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著者	才田 淳治
journal or publication title	Journal of materials research
volume	16
number	11
page range	3046-3049
year	2001
URL	http://hdl.handle.net/10097/47513

doi: 10.1557/JMR.2001.0420

Change in local atomic structure during formation of the icosahedral quasicrystalline phase in $Zr_{70}Pd_{30}$ glassy alloy

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(Received 25 May 2001; accepted 20 August 2001)

The local atomic structures in glassy, supercooled liquid and quasicrystalline phases for a $Zr_{70}Pd_{30}$ binary alloy have been examined by the x-ray diffraction method. It was found that the local atomic structure in the glassy phase can be identified as the distorted icosahedral-like structure around Zr and remains almost unchanged by the phase transformation into the supercooled liquid. In the formation process of the icosahedral phase, approximately one Zr atom substitutes with one Pd atom in this local structure. This kind of atomic rearrangement may improve the perfectibility of the as-quenched icosahedral-like cluster, leading to the phase evolution of the icosahedral phase.

Zr-based alloys such as Zr–Al–TM^{1,2} and Zr–Ti–Al–TM³ (TM = transition metal) are well-known bulk metallic glass formers exhibiting a large supercooled liquid region before crystallization. An icosahedral quasicrystalline phase (*i*-phase) has been often found in the primary crystallization stage of Zr–Al–Ni–Cu⁴ and Zr–Ti–Al–Ni–Cu⁵ glassy alloys containing some amounts of oxygen impurity. Although it has been suggested that the oxygen element stabilizes the formation of the *i*-phase in these alloys, it is difficult to control the amount of oxygen impurity and hence the reproducibility of the formation of the *i*-phase is poor. Recently, reproducible formation of the *i*-phase as a primary precipitation phase has been reported by adding a noble metal (NM) element to Zr–Al–Ni–Cu,⁶ Zr–Al–Ni,⁷ and Zr–Ni⁸ alloys. These results suggest that a complex combination of atomic pairs with strongly large negative heats of mixing (Zr–NM and Zr–Ni) and nearly zero or positive heats of mixing (NM–Ni) contributes to the formation of the *i*-phase by the restraint of the precipitation of a crystalline phase. More recently, the present authors have found the formation of the *i*-phase in $Zr_{70}Pd_{30}$ binary alloy.⁹ It has been suggested that the strong chemical affinity in the Zr–Pd pair leads to stabilization of an icosahedral short-range ordering structure, but little has been obtained about its experimental evidence up to now. This paper is

intended to examine the change in the short-range ordered structure during the phase transformation from a glassy to quasicrystalline phase in the $Zr_{70}Pd_{30}$ alloy and to discuss the structural correlation between these phases.

A glassy alloy ribbon of $Zr_{70}Pd_{30}$ was prepared by the single-roller melt-spinning technique from a $Zr_{70}Pd_{30}$ arc-melted master ingot in an Ar atmosphere. The thermal behavior was analyzed by differential scanning calorimetry (DSC) at a heating rate of 0.67 K s⁻¹. The glassy sample was annealed at various annealing temperatures (T_a) for 120 s in a high-vacuum infrared furnace under the residual pressure less than 10⁻⁴ Pa. The radial distribution function (RDF) was evaluated by the ordinary x-ray diffraction method with monochromatic Mo K_α radiation. The maximum $Q [= 4\pi(\sin \theta)/\lambda]$ value for Fourier transformation was 160 nm⁻¹ in this study. The scattered x-ray intensities were corrected for air-scattering, absorption, and polarization effects and converted to electron units with the generalized Krogh–Moe–Norman method.^{10,11} Further detailed explanation of the experimental procedure was given in some previous papers on various amorphous alloys.^{12,13}

Figure 1(a) shows the DSC curve of the as-quenched glassy $Zr_{70}Pd_{30}$ alloy ribbon. Two exothermic peaks are observed after the appearance of an endothermic one. They correspond to the quasicrystallization and crystallization reactions.⁹ The glass transition temperature (T_g) and the onset temperatures of the first and second exothermic peaks (T_{x1} and T_{x2}) are 686, 717, and 804 K, respectively. The $\Delta T_x (= T_{x1} - T_g)$ is evaluated to be 31 K. The glassy ribbon was annealed for 120 s at 686

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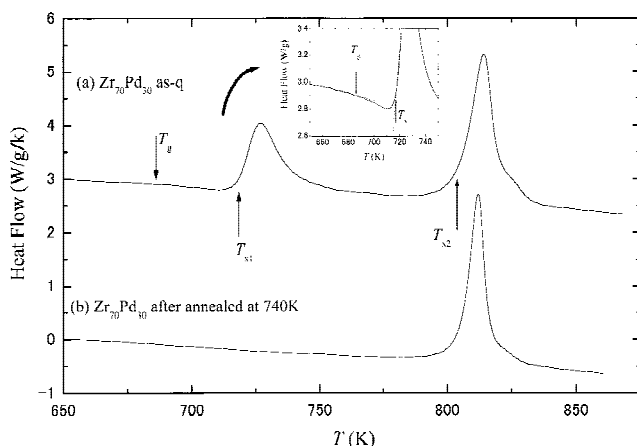


FIG. 1. DSC curves of $Zr_{70}Pd_{30}$ alloys: (a) as-quenched; (b) after annealed for 120 s at 740 K. The heating rate is 0.67 K s^{-1} .

and 740 K to obtain the supercooled liquid and quasicrystalline phases, respectively. The DSC curve of the sample annealed for 120 s at 740 K is also shown in Fig. 1(b). The first exothermic peak around 730 K completely vanishes, and only the second exothermic peak around 812 K is seen. This means that the quasicrystallization reaction is completed accompanying the disappearance of the as-quenched glassy phase by annealing at 740 K for 120 s. Consequently, we examined three types of $Zr_{70}Pd_{30}$ alloy ribbons of glassy (as-quenched), supercooled liquid (annealed at 686 K 120 s), and icosahedral (annealed at 740 K for 120 s) phases.

The densities of the glassy, supercooled liquid, and icosahedral phases measured by the Archimedeian method are 7.71 , 7.72 , and 7.76 Mg/m^3 , respectively. The change in density during the phase transformation from amorphous to i -phase is only about 0.6%. Considering the small change in density less than 1% has been observed for bulk metallic glasses upon crystallization and is attributed to a higher degree of dense random packing state,¹⁴ this implies that the quasicrystallization reaction of $Zr_{70}Pd_{30}$ does not lead to significant change of the dense packing configuration in the glassy phase.

The obtained interference functions (solid curves) of glassy, supercooled liquid, and i -phases for the $Zr_{70}Pd_{30}$ alloy are shown in Fig. 2. The curves of the glassy and supercooled liquid phases are very similar to each other. One can see a shoulder in the second peak as is often observed for various metallic amorphous alloys. On the other hand, several distinct sharp peaks are seen for the i -phase sample. The nonlinear least-squares variation method^{15,16} was used for the fitting calculations of interference functions. The dotted curves in this figure agree with the calculated results by considering the first nearest neighboring shell.

RDF calculated from the Fourier transformation of the interference functions are shown in Fig. 3. The positions of possible atomic pairs in the first neighboring shell are

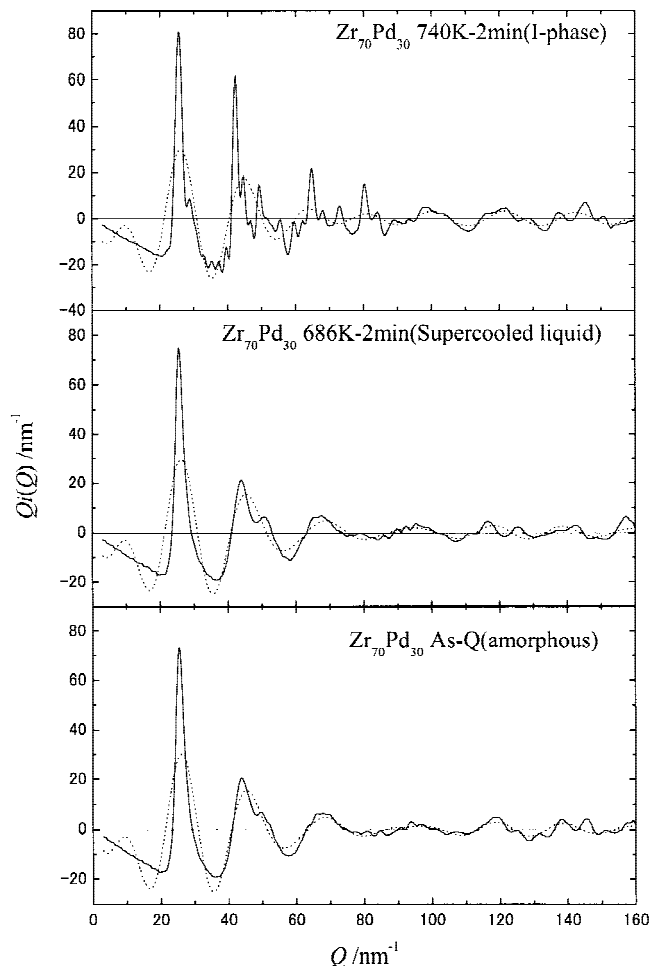


FIG. 2. Interference functions of glassy (as-quenched), supercooled liquid (annealed at 686 K for 120 s), and icosahedral (annealed at 740 K for 120 s) phases. The solid and dotted curves correspond to the experimental and calculated ones, respectively.

also indicated by referring the atomic radius of each element (Zr, 0.160 nm; Pd, 0.137 nm) and the average x-ray weighting factors of atomic pairs (Zr–Zr, 0.39; Zr–Pd, 0.47; Pd–Pd, 0.14). We can see two main peaks corresponding to Zr–Zr and Zr–Pd pairs in the first nearest neighboring shell. The change in RDF due to the phase transformation is summarized in Fig. 4. It is distinct that the local atomic structure of the i -phase is significantly different from that of the glassy phase, whereas the RDF of the supercooled liquid phase is very similar to that of the glassy phase. In particular, the nearest neighboring correlation decreases for a Zr–Pd pair and increases for a Zr–Zr pair by the formation of the i -phase. Several sharp peaks corresponding to the i -phase are also observed at a longer distance side.

The nearest neighboring atomic distances and coordination numbers of the glassy, supercooled liquid, and icosahedral phases are summarized in Table I. The fitting

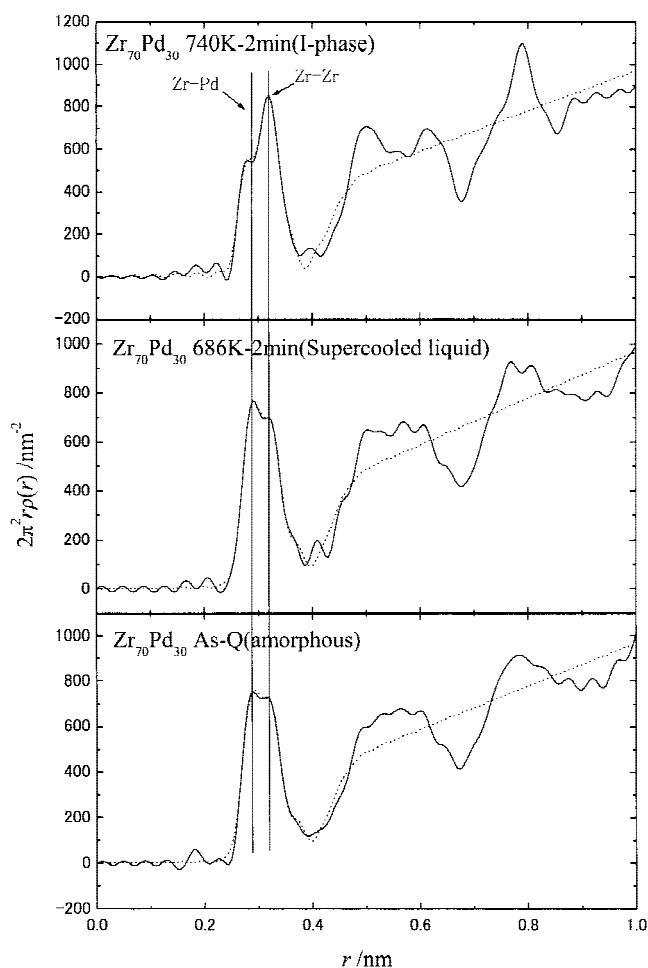


FIG. 3. Radial distribution functions (RDFs) of glassy (as-quenched), supercooled liquid (annealed at 686 K for 120 s), and icosahedral (annealed at 740 K for 120 s) phases. The solid and dotted curves correspond to the experimental and calculated ones, respectively. The positions of Zr–Pd and Zr–Zr pairs in the first nearest neighboring shell are also indicated in this figure.

calculation was derived by the neighboring atoms up to 0.40 nm including the second neighboring Zr–Zr pair (5th line in this table). In this paper, however, we will discuss the local structure with the first nearest Pd–Pd, Zr–Pd, and Zr–Zr pairs. We can see from this table that the structural parameters in the glassy and the super-

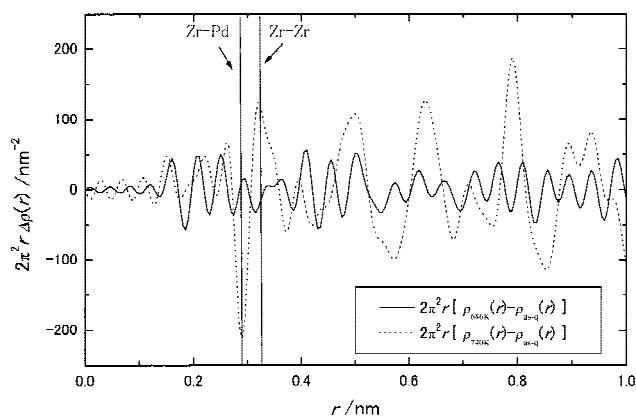


FIG. 4. Change in the RDF after the formation of supercooled liquid and icosahedral phases. The solid and dotted curves correspond to $2\pi^2r[\rho_{686K}(r) - \rho_{as-q}(r)]$ and $2\pi^2r[\rho_{740K}(r) - \rho_{as-q}(r)]$, respectively.

cooled liquid phases remain almost unchanged. This means that the local atomic structure of the supercooled liquid phase is similar to that of the glassy phase. In these phases, the local atomic structure around Zr can be regarded as an icosahedral-like structure because the sum of the coordination numbers around Zr is very close to 12.0 by taking account of the fitting errors. This structure is considered to be distorted to some extent because of the difference in the atomic radii of Zr and Pd. In this structure, the coordination numbers of Zr–Zr and Zr–Pd are about 8.3 and 3.7, respectively, for the glassy phase and about 8.0 and 3.7, respectively, for the supercooled liquid. These values are close to those calculated from the composition of this alloy. Although the total coordination number around Zr for the *i*-phase is 12.3 and is nearly the same as the previous phases, it is again clarified that the drastic change in the local structure occurs through the phase evolution of the *i*-phase. By the formation of the *i*-phase, the coordination number of Zr–Zr pair increases by about 1.5 and that of the Zr–Pd pair decreases by about 1.2 from the glassy phase. On the other hand, the total coordination numbers around Pd in the glassy, supercooled liquid, and icosahedral phases are evaluated to be about 9.2, 9.2, and 6.1, respectively. These results imply that the icosahedral local structure is formed around Zr atom rather than Pd atom. During the

TABLE I. Summary of coordination numbers (N) and interatomic distances (r) for glassy (as-quenched), supercooled liquid (annealed for 120 s at 686 K), and icosahedral (annealed for 120 s at 740 K) $Zr_{70}Pd_{30}$ alloys. The N value for “X–Y” pairs denotes the number of Y atoms around the X atom.

	Amorphous		Supercooled liquid		<i>i</i> -Phase	
	r/nm	N/atom	r/nm	N/atom	r/nm	N/atom
Pd–Pd	0.273 ± 0.002	0.6 ± 0.2	0.276 ± 0.002	0.6 ± 0.2	0.265 ± 0.002	0.3 ± 0.2
Zr–Pd	0.289 ± 0.001	3.7 ± 0.2	0.289 ± 0.001	3.7 ± 0.2	0.281 ± 0.002	2.5 ± 0.2
(Pd–Zr)	(0.289 ± 0.001)	(8.6 ± 0.2)	(0.289 ± 0.001)	(8.6 ± 0.2)	(0.281 ± 0.002)	(5.8 ± 0.2)
Zr–Zr	0.326 ± 0.002	8.3 ± 0.4	0.326 ± 0.002	8.0 ± 0.5	0.320 ± 0.002	9.8 ± 0.6
Zr–Zr	0.368 ± 0.004	2.6 ± 0.4	0.366 ± 0.004	2.6 ± 0.5	0.351 ± 0.004	3.3 ± 0.7

quasicrystallization process, about one Zr atom substitutes with one Pd atom in the distorted icosahedral local structure so as to increase the perfectibility of icosahedral cluster around Zr atom. Consequently, this kind of atomic rearrangement in the icosahedral cluster seems to play a role as the nucleation site for the formation of the *i*-phase.

It has been recognized that the phase transformation to the *i*-phase in the $Zr_{70}Pd_{30}$ alloy takes place by a diffusion-controlled growth mode with increasing nucleation rate.¹⁷ We showed that the interatomic diffusion occurs in a manner of exchanging Pd atom to Zr atom around Zr. In this study, however, the correlation of the Pd–Pd pair is relatively weak and is assumed to correspond to the position of the nearest distance in the first nearest neighboring shell. Further studies, such as anomalous x-ray scattering measurements near the x-ray absorption edges of Zr and Pd, are helpful in performing the more precise analysis in the phase transformation behavior of the $Zr_{70}Pd_{30}$ alloy.

The glassy $Zr_{70}Pd_{30}$ alloy transforms into supercooled liquid and icosahedral quasicrystalline phases during the annealing process. The local atomic structure of this alloy remains almost unchanged during the phase transformation from the glassy phase to supercooled liquid. The local atomic structure around Zr in both phases is characterized as a distorted icosahedral structure surrounded by average numbers of Zr and Pd atoms expected from the composition. During the quasicrystallization stage, approximately one Zr atom substitutes for one Pd atom in this local structure. This kind of modification in the local

atomic structure improves the perfectibility of the icosahedral-like structure and is concluded to be essential for the quasicrystallization of the $Zr_{70}Pd_{30}$ alloy.

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