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Evidence of polymorphous amorphous-to-quasicrystalline phase transformation in Zr$_{66.7}$Pd$_{33.3}$ metallic glass

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The amorphous-to-quasicrystalline phase transformation and the pressure effect on the transformation in a Zr$_{66.7}$Pd$_{33.3}$ metallic glass have been investigated by in situ x-ray diffraction measurements using synchrotron radiation. It is found that the transformation is a polymorphous reaction and external pressure enhances the onset temperature for the formation of quasicrystals with a rate of 22 K/GPa while the temperature interval for the stability of quasicrystals remains almost unchanged in the pressure range of 0–4 GPa. The enhancement of the onset temperature for the formation of quasicrystals has been further discussed with the nucleation theory. © 2002 American Institute of Physics. [DOI: 10.1063/1.1447015]

Recently, after the discovery of the formation of quasicrystals from Zr–Al–Cu–Ni metallic glasses, quasicrystals have been found to form upon crystallization in many Zr-based alloy systems, such as ZrM (M = Pd and Pt), ZrNiM (M = Pd, Au, Pt, and Ti), ZrCuM (Al and Pd), ZrAlCuPd, ZrCuNiPd, ZrAlNiM (M = Cu, Pd, Au, and Pt), ZrCuTiNi, ZrAlNiCuM (M = Ti, Au, Pt, Pd, and Ag), ZrTiCuNiBe, and ZrTiNbCuNiAl. Furthermore, Inoue and co-workers found that bulk quasicrystalline ZrAlNiCuM (M = Pd and Ag) alloys exhibit high strength and good ductility. Hence, the formation of quasicrystals in these alloys becomes very interesting. However, the mechanism of the amorphous-to-quasicrystalline transformation is not completely understood. In the ZrAlNiCuAg system, Chen et al. suggested a polymorphous transformation while Lee et al. reported that formation of quasicrystalline phase may involve partitioning of solute. Furthermore, Jiang et al. suggested that atomic mobility is important for the time-dependent nucleation of quasicrystals in the metallic glass. In the ZrAlNiCuPd system, Inoue et al. reported a diffusion controlled amorphous-to-quasicrystalline transformation. In the binary Zr$_{70}$Pd$_{30}$ system, Saida, Matsushita, and Inoue studied the transformation kinetic by differential scanning calorimetry and found that the transformation is also diffusion controlled, while Murty, Ping, and Hono suggested that the composition of the quasicrystals is close to 70 at. % Zr. Both groups found that the quasicrystals formed in the ZrPd system transform into an intermetallic Zr$_5$Pd compound at high temperature. Thus, the composition of Zr$_{66.7}$Pd$_{33.3}$ becomes of particular interest to clarify the nature of the amorphous-to-quasicrystalline phase transformation. If the transformation processes, amorphous-to-quasicrystalline-to-Zr$_5$Pd, occur in the Zr$_{66.7}$Pd$_{33.3}$ metallic glass, then the amorphous-to-quasicrystalline transformation is most likely a polymorphous reaction because the starting amorphous alloy has the same composition as the final intermetallic compound. In this work, we investigate the origin of the amorphous-to-quasicrystalline phase transformation in the Zr$_{66.7}$Pd$_{33.3}$ metallic glass by in situ high-temperature x-ray diffraction (XRD) measurements using synchrotron radiation. The pressure effect on the crystallization temperature of the glass has also been investigated.

A ribbon sample of the Zr$_{66.7}$Pd$_{33.3}$ metallic glass with a cross section of 0.03 mm × 1 mm was prepared by the melt-spinning technique from a master alloy ingot prepared by arc melting in an Ar atmosphere. The amorphous nature of the as-quenched ribbon was confirmed by x-ray powder diffraction and transmission electron microscopy. Thermal analysis was performed in a differential scanning calorimeter (DSC) at a heating rate of 40 K/min under a flow of purified argon. As shown in Fig. 1, the alloy exhibits an endothermic event characteristic of the glass transition, followed by two characteristic exothermic events indicating a two-stage phase transformation process. It was found that the glass transition temperature $T_g$, estimated as the onset temperature of the glass transition event, is 711 K, the onset temperatures and the exothermic heats of the first and second crystallization events, $T_{x1} = 750$ K, $T_{x2} = 796$ K and 28.7, 29.6 J/g, respectively, $\Delta T = T_{x1} - T_g = 39$ K, and $T_{x2} - T_{x1} = 46$ K. The proximity of the two exothermic peaks requires fast time-resolved XRD measurements to monitor the phase transformations in the Zr$_{66.7}$Pd$_{33.3}$ metallic glass.

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In situ high-temperature x-ray diffraction measurements using synchrotron radiation at HASYLAB in Hamburg, Germany, were performed in two modes: (1) angle-dispersive x-ray diffraction (ADXRD) in vacuum at beamline Petra1 using a wavelength of 0.56354 Å and an image plate detector for 1 min exposure of each pattern and (2) energy-dispersive high-pressure x-ray diffraction (EDXRD) at beamline MAX80 using a multi-anvil pressure apparatus for 20 min exposure of each pattern. For ADXRD measurements, ribbon samples were installed in a vacuum chamber of 2 × 10⁻⁵ Torr and were heated by Joule heating. The sample temperature was measured by a pyrometer. The temperature stability is approximately ± 10 K while the absolute sample temperature has a larger uncertainty. For EDXRD measurements up to about 4 GPa, electric current was sent through a graphite heater via two appropriate anvils. The temperature was measured by means of a thermocouple with a stability of ± 1 K. Each run consists of an isothermal room-temperature compression followed by an isobaric heating to high temperature in steps of 10 K. The average heating rate in the temperature range from 298 to 873 K was roughly estimated to be 3 K/min. The pressure of the sample is calculated from the lattice constant of NaCl using the Decker equation of state. Pure Zr, Fe, and the metallic glass were used to examine the possible oxidation of samples during the heat treatments using the sample assembly. For the three systems, only pure metallic phases were detected after heat treatments at temperatures up to 873 K.

Figure 2 shows time-resolved ADXRD patterns of the Zr₆₆.₇Pd₃₃.₃ metallic glass at a given temperature. It is clear that after 1 min the sample is still amorphous while the XRD pattern recorded after 4 min shows some broad diffraction peaks which can be indexed with a primitive icosahedral structure. No intermetallic Zr₂Pd compound was detected. In the XRD pattern recorded after 5 min, a tiny intermetallic Zr₂Pd compound appears together with the quasicrystalline phase. After 7 min the pattern is dominated by the intermetallic compound and single Zr₂Pd phase remains in XRD patterns recorded longer than 10 min. The amorphous-to-quasicrystalline-to-intermetallic Zr₂Pd phase transformation sequence was indeed detected at different temperatures for the Zr₆₆.₇Pd₃₃.₃ metallic glass. These results clearly reveal that the amorphous-to-quasicrystalline phase transformation in the Zr₆₆.₇Pd₃₃.₃ metallic glass is a polymorphous reaction. No long-range atomic diffusion is required for the phase transformation in the glass.

In situ high-temperature EDXRD measurements of the Zr₆₆.₇Pd₃₃.₃ metallic glass were performed in a pressure range of 0–4 GPa. EDXRD patterns were recorded every 10 K in order to observe the onset temperature of crystallization within an uncertainty of 10 K. The crystalline phases determined from the EDXRD patterns recorded are identical in the pressure range used. Figure 3 exemplifies EDXRD patterns recorded for the sample at 2.5 GPa and various temperatures. A broad amorphous peak, located at $E \approx 51$ keV, together with a few Bragg peaks from BN, are observed in the EDXRD patterns recorded at low temperatures. At 763 K, new Bragg peaks appear and become much clearer in the pattern recorded at 773 K. The quasicrystalline phase is marked with the arrows. At 813 K only intermetallic Zr₂Pd compound remains. The existence of intermetallic Zr₂Pd compound along with quasicrystals at low temperatures is due to the fast kinetic of the quasicrystalline-to-intermetallic compound transformation, as shown in Fig. 2. Figure 4

FIG. 2. In situ high-temperature time-resolved x-ray diffraction patterns recorded at a given temperature for various times of the Zr₆₆.₇Pd₃₃.₃ metallic glass with a wavelength of 0.56354 Å. Exposure time is 1 min for each XRD pattern. All diffraction peaks in the pattern recorded after 10 min are indexed to intermetallic compound Zr₂Pd.

FIG. 3. In situ energy-dispersive x-ray diffraction patterns recorded at 2.5 GPa for the Zr₆₆.₇Pd₃₃.₃ metallic glass at various temperatures (Ed = 122.166 keV Å). Exposure time is 20 min for each XRD pattern. Some diffraction peaks of boron nitride originating from the sample holder are marked by BN.
shows the onset temperatures for appearing, $T_1$, and disappearing, $T_2$, of the quasicrystalline phase in the Zr$_{66.7}$Pd$_{33.3}$ metallic glass as a function of pressure. The solid lines represent the linear fit to the data.

For the polymorphous crystallization process in the Zr$_{66.7}$Pd$_{33.3}$ metallic glass, the onset temperature of the amorphous-to-quasicrystalline phase transformation may be governed by the thermodynamic potential energy barrier of nucleation. Therefore, it is expected that the onset temperature of the amorphous-to-quasicrystalline phase transformation in the Zr$_{66.7}$Pd$_{33.3}$ metallic glass increases with pressure, as observed in Fig. 4.

In conclusion, the amorphous-to-quasicrystalline phase transformation and the pressure effect on the transformation in the Zr$_{66.7}$Pd$_{33.3}$ metallic glass have been investigated by in situ x-ray diffraction measurements using synchrotron radiation. It is found that the transformation is a polymorphous reaction and external pressure enhances the onset temperature for the formation of quasicrystals with a rate of 22 K/GPa while the temperature interval for the stability of quasicrystals remains almost unchanged in the pressure range of 0–4 GPa.