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# Evidence of polymorphous amorphous-to-quasicrystalline phase transformation in $Zr_{66.7}Pd_{33.3}$ metallic glass

J. Z. Jiang<sup>a)</sup> and K. Saks

*Department of Physics, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark*

J. Saida

*Inoue Superliquid Glass Project, ERATO, Japan Science and Technology Corporation (JST), Sendai 982-0807, Japan*

A. Inoue

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

H. Franz, K. Messel, and C. Lathe

*HASYLAB am DESY, Notkestrasse 85, D-22603 Hamburg, Germany.*

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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,<sup>1</sup> quasicrystals have been found to form upon crystallization in many Zr-based alloy systems, such as ZrM (M=Pd and Pt),<sup>2,3</sup> ZrNiM (M=Pd, Au, Pt, and Ti),<sup>4,5</sup> ZrCuM (Al and Pd),<sup>6,7</sup> ZrAlCuPd,<sup>7</sup> ZrCuNiPd,<sup>7</sup> ZrAlNiM (M=Cu, Pd, Au, and Pt),<sup>1,8–10</sup> ZrCuTiNi,<sup>11</sup> ZrAlNiCuM (M=Ti, Au, Pt, Pd, and Ag),<sup>7,12–17</sup> ZrTiCuNiBe,<sup>18</sup> and ZrTiNbCuNiAl.<sup>19</sup> Furthermore, Inoue and co-workers<sup>16</sup> 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.*<sup>15</sup> suggested a polymorphous transformation while Lee *et al.*<sup>17</sup> reported that formation of quasicrystalline phase may involve partitioning of solute. Furthermore, Jiang *et al.*<sup>20</sup> suggested that atomic mobility is important for the time-dependent nucleation of quasicrystals in the metallic glass. In the ZrAlNiCuPd system, Inoue *et al.*<sup>16</sup> reported a diffusion controlled amorphous-to-quasicrystalline transformation. In the binary  $Zr_{70}Pd_{30}$  system, Saida, Matsushita, and Inoue<sup>2</sup> studied the transformation kinetic by differential scanning calorimetry and found that the transformation is also diffusion controlled, while Murty, Ping, and Hono<sup>3</sup> 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  $Zr_2Pd$  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- $Zr_2Pd$ , 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.

<sup>a)</sup>Author to whom all correspondence should be addressed: electronic mail: jiang@fysik.dtu.dk

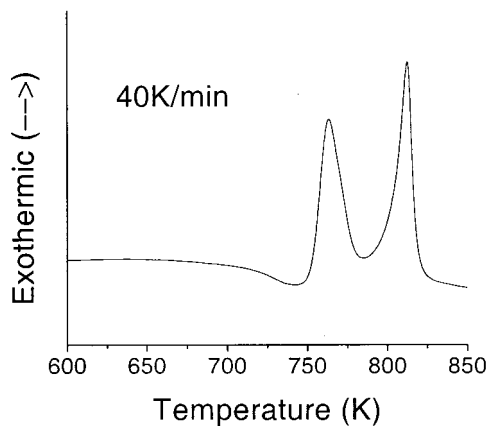


FIG. 1. DSC curve of the  $Zr_{66.7}Pd_{33.3}$  metallic glass at a heating rate of 40 K/min under a flow of purified argon.

*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 Petra4 using a wavelength of  $0.56354 \text{ \AA}$  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.<sup>21</sup> For ADXRD measurements, ribbon samples were installed in a vacuum chamber of  $2 \times 10^{-5}$  Torr and were heated by Joule heating. The sample temperature was measured by a pyrometer. The temperature stability is approximately  $\pm 10$  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 voltage with a stability of  $\pm 1$  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

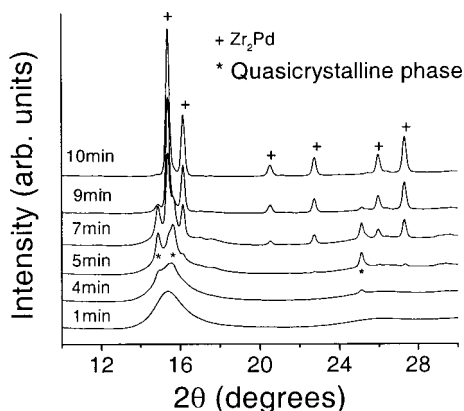


FIG. 2. *In situ* high-temperature time-resolved x-ray diffraction patterns recorded at a given temperature for various times of the  $Zr_{66.7}Pd_{33.3}$  metallic glass with a wavelength of  $0.56354 \text{ \AA}$ . Exposure time is 1 min for each XRD pattern. All diffraction peaks in the pattern recorded after 10 min are indexed to intermetallic compound  $Zr_2Pd$ .

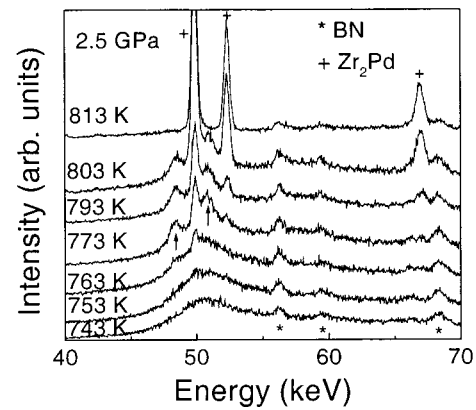


FIG. 3. *In situ* energy-dispersive x-ray diffraction patterns recorded at 2.5 GPa for the  $Zr_{66.7}Pd_{33.3}$  metallic glass at various temperatures ( $E_d = 122.166 \text{ keV \AA}$ ). Exposure time is 20 min for each XRD pattern. Some diffraction peaks of boron nitride originating from the sample holder are marked by BN.

Decker equation of state.<sup>22</sup> 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  $Zr_{66.7}Pd_{33.3}$  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.<sup>18,23</sup> No intermetallic  $Zr_2Pd$  compound was detected. In the XRD pattern recorded after 5 min, a tiny intermetallic  $Zr_2Pd$  compound appears together with the quasicrystalline phase. After 7 min the pattern is dominated by the intermetallic compound and single  $Zr_2Pd$  phase remains in XRD patterns recorded longer than 10 min. The amorphous-to-quasicrystalline-to-intermetallic  $Zr_2Pd$  phase transformation sequence was indeed detected at different temperatures for the  $Zr_{66.7}Pd_{33.3}$  metallic glass. These results clearly reveal that the amorphous-to-quasicrystalline phase transformation in the  $Zr_{66.7}Pd_{33.3}$  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  $Zr_{66.7}Pd_{33.3}$  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  $E \approx 51 \text{ keV}$ , 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  $Zr_2Pd$  compound remains. The existence of intermetallic  $Zr_2Pd$  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

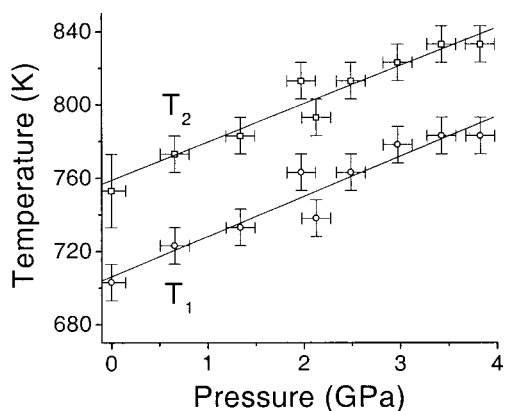


FIG. 4. Onset temperatures for appearing,  $T_1$ , and disappearing,  $T_2$ , of the quasicrystalline phase in the  $Zr_{66.7}Pd_{33.3}$  metallic glass as a function of pressure. The solid lines represent the linear fit to the data.

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. It is clear that  $T_1$  and  $T_2$  increase with pressure having a slope of 22 K/GPa while the temperature interval,  $T_2 - T_1$ , remains almost unchanged around 50 K in the pressure range used. The slope of 22 K/GPa is similar to literature data reported for metallic glasses with a wide supercooled liquid region, e.g., 19 K/GPa for the  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  bulk glass<sup>24</sup> in the pressure range of 0–4 GPa, 30 K/GPa for the  $Fe_{72}P_{11}C_6Al_5B_4Ga_2$  glass<sup>25</sup> in the pressure range of 0–2.4 GPa, 11 K/GPa for the  $Pd_{40}Cu_{30}Ni_{10}P_{20}$  bulk glass<sup>26</sup> in the pressure range of 0–4 GPa, 9.5 K/GPa for the  $Zr_{48}Nb_8Cu_{14}Ni_{12}Be_{18}$  bulk glass<sup>27</sup> in the range of 0–4.4 GPa, and 16 K/GPa for the  $Mg_{60}Cu_{30}Y_{10}$  bulk glass in the pressure range 0–4 GPa.<sup>28</sup> Note that the  $T_1$  (or  $T_2$ ) differs from  $T_{x1}$  (or  $T_{x2}$ ), which could be due to (1) different heating rates used and (2) different techniques used.

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. According to crystallization kinetics theory, the nucleation rate,  $I$ , can be written as  $I = I_0 / \exp(\Delta G^* / k_B T)$ , where  $I_0$  is a constant,  $k_B$  is Boltzmann's constant, and  $\Delta G^*$  is the free energy required to form a nucleus of the critical size, i.e., the thermodynamic potential energy barrier of nucleation,  $\Delta G^* \propto 1 / (P\Delta V + \Delta G)^2$ , where  $\Delta V$  and  $\Delta G$  are the changes of molar volume and free energy from amorphous to quasicrystalline phase. Based on the observation in Fig. 2, it is not unreasonable to expect  $\Delta G = G_{quasi} - G_{amor} < 0$ . Moreover, Holzer and Kelton<sup>29</sup> reported that the densities of the amorphous and quasicrystalline  $Al_{75}Cu_{15}V_{10}$  phase are  $3.92 \pm 0.04$  and  $3.79 \pm 0.06$  g/cm<sup>3</sup>, respectively. Their result indicates a larger molar volume for the quasicrystalline phase than the corresponding amorphous phase. Assuming the same behavior for the  $Zr_{66.7}Pd_{33.3}$  metallic glass,  $\Delta V = V_{quasi} - V_{amor} > 0$ .  $(P\Delta V + \Delta G)^2$  could be smaller than  $(\Delta G)^2$  with increasing pressure from ambient condition to 4 GPa. Consequently, the external pressure applied enhances the thermodynamic potential energy barrier of nucleation. Therefore, it is expected that the onset tem-

perature 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.

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