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Pressure effect on crystallization temperature in $Zr_{70}Pd_{30}$ metallic glass

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The pressure effect on amorphous-to-quasicrystalline-to-intermetallic phase transformations in a $Zr_{70}Pd_{30}$ metallic glass has been investigated by *in situ* x-ray diffraction measurements using synchrotron radiation. It is found that the glass crystallizes in two steps: (1) amorphous-to-icosahedral quasicrystalline and (2) icosahedral quasicrystalline-to-intermetallic $Zr_{2+x}Pd$ alloy. The intermetallic alloy has a tetragonal structure with lattice parameters, $a = 3.310(1)$ Å and $c = 10.974(1)$ Å, and a space group of I4/mmm. External pressure enhances the onset temperatures for the formation of quasicrystalline phase and intermetallic compound with rates of 11 ± 3 and 9 ± 4 K/GPa, respectively, while the temperature interval for the stability of quasicrystals remains almost unchanged in the pressure range of 0–3 GPa. External pressure does not affect the phase-selection sequence. The enhancement of the onset temperature for the formation of quasicrystals has been further discussed with the nucleation theory. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1655684]

INTRODUCTION

Recently, after the discovery of the formation of quasicrystals from Zr–Al–Cu–Ni metallic glasses,[1] quasicrystals have been found to form upon crystallization in many Zr-based alloy systems, such as ZrM (M = Pd and Pt),[2,3] ZrNiM (M = Pd, Au, Pt, and Ti),[4,5] ZrCuM (Al and Pd),[6,7] ZrAlCuPd,[7] ZrCuNiPd,[7] ZrAlNiM (M = Cu, Pd, Au, and Pt),[1,8–10] ZrCuTiNi,[11] ZrAlNiCuM (M = Ti, Au, Pt, Pd, and Ag),[7,12–17] ZrTiCuNiBe,[18] and ZrTiNbCuNiAl.[19] Furthermore, Inoue and coworkers[16] 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.*[13] suggested a polymorphous transformation while Lee *et al.*,[17] reported that formation of the quasicrystalline phase may involve partitioning of solutes. Jiang *et al.*,[20] suggested that atomic mobility is important for the time-dependent nucleation of quasicrystals in the metallic glass and the authors further revealed changes in quasilattice parameter and composition during the amorphous-to-quasicrystalline phase transformation.[21] The structural stability of the quasicrystals formed in the metallic glass was also reported up to a hydrostatic pressure of 28 GPa.[22] In the ZrAlNiCuPd system, Inoue *et al.*[16] reported a diffusion controlled amorphous-to-quasicrystalline transformation. In the binary $Zr_{70}Pd_{30}$ system, Saida *et al.*[2] studied the transformation kinetics by differential scanning calorimetry (DSC) and found that the transformation is also diffusion controlled while Murty *et al.*[3] suggested that the composition of the quasicrystals is close to 70 at. % Zr. Very recently, both groups reported partitioning during the amorphous-to-quasicrystalline phase transformation in the alloy.[23,24] They found that the quasicrystals formed in the ZrPd system transform into an intermetallic Zr_2Pd compound at high temperature.[23,24] Jiang *et al.*[25] demonstrated that the amorphous-to-quasicrystalline in the $Zr_{66.7}Pd_{33.3}$ metallic glass is a polymorphous reaction. Here, we report on the pressure effect on amorphous-to-quasicrystalline-to-intermetallic phase transformations in the $Zr_{70}Pd_{30}$ metallic glass by in-situ high-pressure and high-temperature x-ray diffraction (XRD) measurements using synchrotron radiation.

EXPERIMENT

A ribbon sample of the $Zr_{70}Pd_{30}$ 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 by DSC at a heating rate of 40 K/min under a flow of purified argon.

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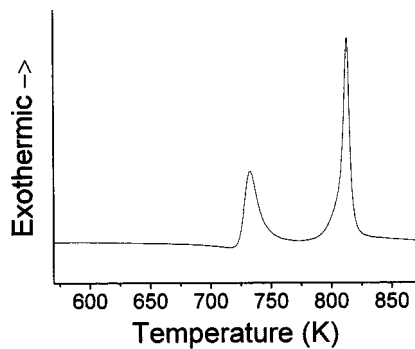
FIG. 1. The DSC curve of the $Zr_{70}Pd_{30}$ metallic glass at a heating rate of 40 K/min under a flow of purified argon.

FIG. 2. Room-temperature x-ray powder diffraction patterns recorded for $Zr_{70}Pd_{30}$ samples annealed in vacuum 1×10^{-4} mbar at 703, 723, and 803 K for 10 min using Cu K_α radiation.

In situ high-pressure and high-temperature x-ray diffraction measurements using synchrotron radiation at HASYLAB in Hamburg, Germany, were performed by energy-dispersive high-pressure x-ray diffraction (EDXRD) at beamline MAX80 using a multianvil pressure apparatus for 5 min exposure of each pattern.[26] For EDXRD measurements up to about 3 GPa, 8 mm cube pressure cells, which were compressed by six truncation anvils of tungsten carbide in a 250-ton hydraulic press, were used. 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 ± 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.[27] Pure Zr, Fe, and the metallic glass were used to examine possible oxidation of the 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.

RESULTS AND DISCUSSION

Figure 1 shows a DSC curve for the $Zr_{70}Pd_{30}$ metallic glass. 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 701 K, the onset temperatures and the exothermic heats of the first and second crystallization event, $T_{x1} = 723$ K, $T_{x2} = 799$ K, and 21.4 J/g and 38.3 J/g, respectively, $\Delta T = T_{x1} - T_g = 22$ K, and $T_{x2} - T_{x1} = 76$ K. The structural evolution was further studied by room-temperature XRD for the samples annealed in 1×10^{-4} mbar vacuum at 703, 723, and 803 K for 10 min using Cu Kα radiation, as shown in Fig. 2. It is clear that after annealing at 703 K, nanometer-sized quasicrystals are formed in the sample. At 723 K, the intensities of diffraction peaks for the quasicrystalline phase increase while a residual amorphous component still exists. At 803 K, a Zr_2Pd-like phase (tetragonal structure with a space group of I4/mmm) is dominant, indicating the quasicrystalline and residual amorphous phases transform to
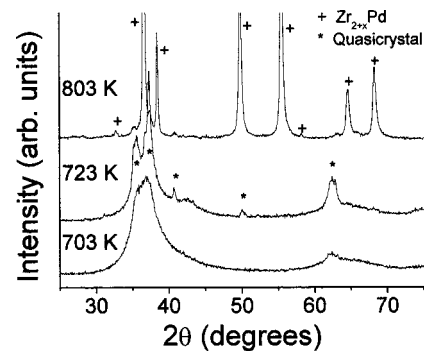
the intermetallic compound. No other crystalline phases were detected with an experimental uncertainty of 3%. We analyzed the diffraction pattern and found the lattice parameters for the intermetallic compound of $a = 3.310(1)$ Å and $c = 10.974(1)$ Å. By comparing them with a pure Zr_2Pd phase, $(a = 3.306$ Å and $c = 10.894$ Å),[28] it is found that the c-axis largely expands while the a-axis only slightly does. This could be caused by substitution of large-size Zr atoms on Pd atomic positions in the tetragonal structure. Thus, the composition of the intermetallic compound might deviate from the stoichiometry to be approximately $Zr_{2+x}Pd$ ($x \approx 0.3$).

In situ high-temperature EDXRD measurements of the $Zr_{70}Pd_{30}$ metallic glass were performed in a pressure range of 0–3 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 0.8 GPa and various temperatures. A broad amorphous peak, located at $E \approx 50$ keV, together with a few Bragg peaks from BN are observed in the EDXRD patterns recorded at low temperatures up to 703 K. At 713 K, broad Bragg peaks appear and become much clearer in the pattern recorded at 733 K. They are from the quasicrystalline phase. At 753 K the intermetallic compound
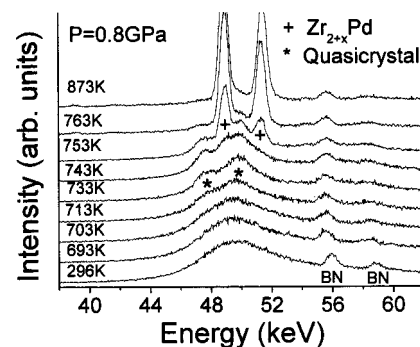

FIG. 3. *In situ* energy-dispersive x-ray diffraction patterns recorded at 0.8 GPa for the $Zr_{70}Pd_{30}$ metallic glass at various temperatures (Ed=121.658 keV Å). Exposure time is 5 min for each XRD pattern. Some diffraction peaks of boron nitride originating from the sample holder are marked by BN.
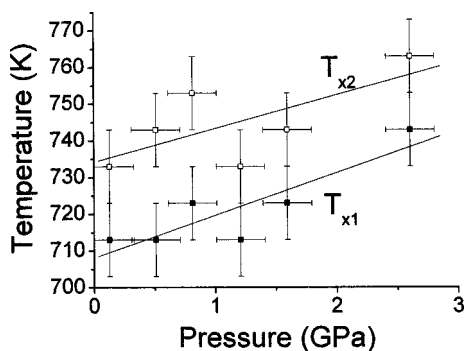
FIG. 4. Onset temperatures for quasicrystalline phase T_{x1} and intermetallic compound T_{x2} in the $Zr_{70}Pd_{30}$ metallic glass as a function of pressure. The solid lines represent the linear fit to the data.

appears while at 873 K only the intermetallic compound was detected. Figure 4 shows the onset temperatures for quasi-rystalline phase, T_{x1}, and for intermetallic compound T_{x2}, as a function of pressure. It is clear that T_{x1} and T_{x2} increase with pressure having slopes of 11 ± 3 and 9 ± 4 K/GPa, respectively. The slopes obtained here are similar to literature data reported for metallic glasses with a wide super-cooled 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[29] in the pressure range of 0–4 GPa, 30 K/GPa for the $Fe_{72}P_{11}C_6Al_5B_4Ga_2$ glass[26] in the pressure range of 0–2.4 GPa, 11 K/GPa for the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ bulk glass[30] 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[31] 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.[32] Note that the crystallization temperatures deduced from DSC and XRD are slightly different, which could be due to (1) different heating rates used and (2) different techniques used.

For the crystallization process in the $Zr_{70}Pd_{30}$ 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 $I = I_0/\exp((\Delta G^* + Q_n)/k_BT)$, where I_0 is a constant, k_B is Boltzmann's constant, Q_n is the activation energy for the transport of an atom across the interface of an embryo, and ΔG^* 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 ΔV and ΔG are the changes of molar volume and free energy from amorphous to quasicrystalline phase. The sum, $\Delta G^* + Q_n$, is called the nucleation work. In general, pressure could reduce atomic mobility. This means that Q_n might increase with pressure. Based on the observation in Fig. 2, it is not unreasonable to expect $\Delta G = G_{quasi} - G_{amor} < 0$. More-over, Holzer and Kelton[33] reported that the densities of the amorphous and quasicrystalline $Al_{75}Cu_{15}V_{10}$ phase are 3.92 ± 0.04 and 3.79 ± 0.06 g/cm^3, respectively. Their result indi-cates a larger molar volume for the quasicrystalline phase than the corresponding amorphous phase. Assuming the same behavior for the $Zr_{70}Pd_{30}$ 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 3 GPa.

Consequently, the external pressure applied enhances the thermodynamic potential energy barrier of nucleation. Hence, the nucleation work increases with pressure. Conse-quently, it is expected that the onset temperature of the amorphous-to-quasicrystalline phase transformation in the $Zr_{70}Pd_{30}$ metallic glass increases with pressure, as observed in Fig. 4. For the quasicrystalline-to-intermetallic phase tran-sition, ΔG^* should decrease with pressure because of nega-tive ΔV and ΔG. However, we experimentally observed an increase of T_{x2} with pressure. This means that the nucleation work increases with pressure, which indicates that Q_n, which is dominant, might increase with pressure.

CONCLUSIONS

In conclusion, the pressure effect of the amorphous-to-quasicrystalline-to-intermetallic phase transformations in the $Zr_{70}Pd_{30}$ metallic glass has been investigated by *in situ* x-ray diffraction measurements using synchrotron radiation. It is found that external pressure does not affect the phase-selection sequence. But, it enhances the onset temperatures for the formation of quasicrystalline phase and intermetallic compound with rates of 11 ± 3 and 9 ± 4 K/GPa, respectively, while the temperature interval for the stability of quasicrys-tals remains almost unchanged in the pressure range of 0–3 GPa.

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