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Effects of Annealing on Structural Evolution and Microhardness of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) Bulk Metallic Glasses and Composites

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Abstract. Effects of annealing on structural evolution and microhardness of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) bulk metallic glasses (BMGs) and composites were investigated using X-ray diffraction (XRD) and micro-hardness analysis. The glass transition temperature T_g and the crystallization temperature T_x of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) BMGs are 703-728 K and 758-764 K, respectively, determined from differential scanning calorimetry (DSC) with heating rate of 10 K/min. The BMG samples were annealed at different temperatures (below T_g, between T_g and T_x, and above T_x) and for different time period (5 min, 10 min, 20 min, 30 min), and then cooled in air. Based on XRD analysis, the as-cast BMG samples and the samples annealed at 623 K (i.e. below T_g) showed amorphous structures, and the samples annealed at 723-923 K (i.e. above T_g) for 30 min showed amorphous-crystalline composite structures. Microhardness measurements indicated that with increasing annealing temperature, microhardness gradually increased and then leveled off.

Introduction

There are no long range order, no dislocations, and no grain boundaries in Bulk metallic glasses (BMGs). They have attracted a lot of interest all over the world because of their large elastic limit (around 2%), high strength, good corrosion and wear resistance, superplasticity and near net-shape fabrication capability in the supercooled liquid region (i.e. between the glass transition temperature T_g and the liquidus temperature T_l)[1-6] . Zr-based BMGs are of special interest due to their good glass forming ability (GFA) and promising applications as structural and functional materials[6-17]. However, their ductility at room temperature needs to be improved. Bulk metallic glass composites (BMGCs) are among the options to improve the ductility, and they can be formed in situ or ex-situ[3-5]. Heat treatment is one of the methods to obtain the BMGCs in situ, and it has important effects on the microstructures, mechanical properties, corrosion and electrochemical properties[10-17]. In this work, effects of annealing temperature and annealing time on the microstructure evolution and microhardness of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) BMGs were investigated.

Experimental details

Sample Preparation. $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) BMGs were prepared by ladle-hearth type arc-melt tilt-casting method[6-8]. Cylindrical ingots with diameter of 8 mm were obtained by arc-melting mixtures of pure Zr, Cu, Al and Pd in an argon atmosphere. SYJ-160 low speed diamond cutting machine with Al_2O_3 annular saw was used to cut the cylindrical samples into slices with thickness of 3 mm at the speed of 150 rpm with distilled water as the coolant.

Differential Scanning Calorimetry. Thermal properties of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) BMGs were investigated using Differential scanning calorimetry (DSC) - PYRIS 1DSC, with heating rate of 10 K/min between 298 K and 973 K, and the sample mass was around 20 mg. The glass transition temperature T_g and the crystallization temperature T_x of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) were determined.

Annealing. Samples of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) BMGs were annealed at different temperatures (below T_g, between T_g and T_x, and above T_x) for different time periods (5 min, 10 min, 20 min and 30 min) in heat treatment furnaces (SX-5-12), and then cooled in air.
X-ray Diffraction and Microhardness Analysis. The as-cast samples and the annealed samples of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) were ground using SiC sand papers (#1200) and polished using polishing cloth with diamond paste (grades of 1.5 to 0.5 micron). X-ray diffraction (XRD) was used to investigate the structures of the as-cast samples and the annealed samples, with diffraction angle of 20-90° and scanning for 30 min. Microhardness analysis was carried out for the as-cast samples and the annealed samples, and a load of 200 g was applied and held for 10 s.

Results and discussions

Differential Scanning Calorimetry. Fig. 1 shows DSC curves of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 5, 9, 12, 15) with heating rate of 10 K/min.[6] As listed in Table 1, $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 5, 9, 12, 15) has glass transition temperature T_g of 703-728 K, and crystallization temperature T_x of 758-764 K. These results are consistent with those reported by Wang et al. for $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 1, 2, 3, 5, 7) with T_g of 690-708 K and T_x of 776-780 K determined by DSC with heating rate of 20 K/min [7].

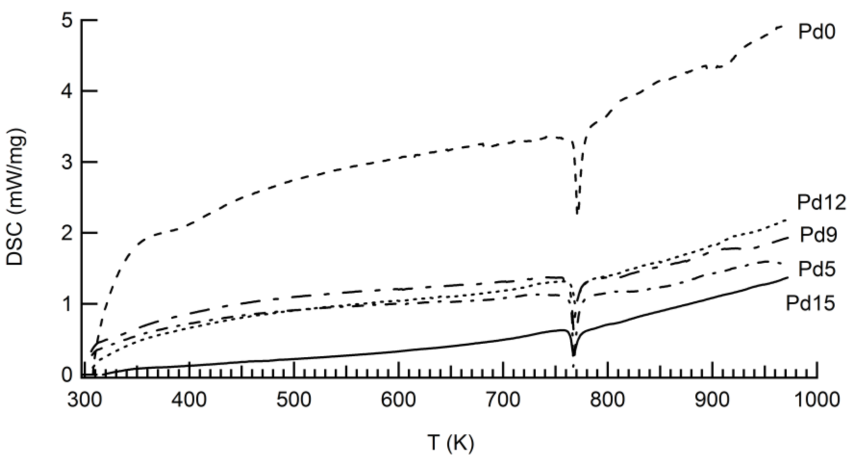


Fig. 1 DSC curves of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 5, 9, 12, 15) with heating rate of 10 K/min

Tab. 1 Glass transition temperature T_g and crystallization temperature T_x of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 5, 9, 12, 15) determined from DSC with heating rate of 10 K/min, compared with results in literature[7] with heating rate of 20 K/min

Pd (at%)	0	1	2	3	5	7	9	12	15
T_g (K)	728				703		712	714	724
T_x(K)	764				758		759	762	761
T_g (K) in [7]	690	701	704	704	707	708			
T_x(K) in [7]	780	780	780	780	776	777			

X-ray Diffraction and Microhardness Analysis. Fig. 2 shows the XRD spectra of the annealed $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=5) samples held at 823 K (i.e. above T_x of 758 K) for different time periods (5 min, 10 min, 20 min and 30 min, respectively). When the sample was held at 823 K for 5 min, amorphous structure remained, indicated by the broad peak. When the sample was held at 823 K for 10-30 min, crystals appeared, indicated by the sharp diffraction peaks, suggesting that the amorphous-crystalline composite structure was obtained.

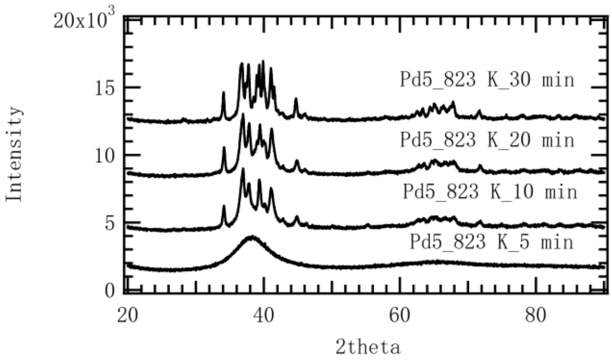
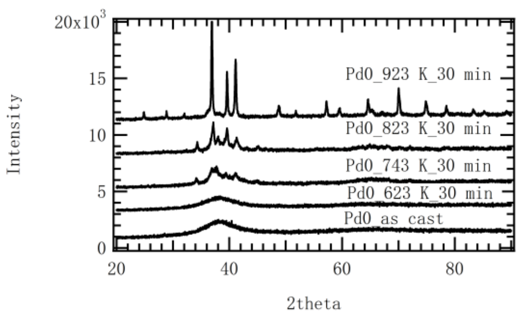
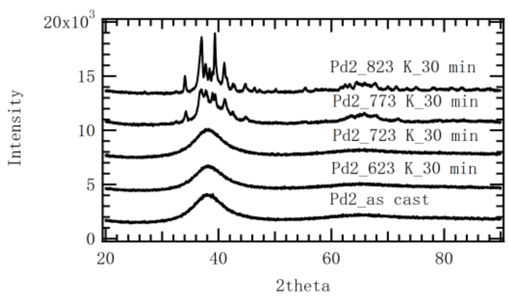


Fig. 2 XRD spectra of the annealed $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=5) samples held at 823 K for 5 min, 10 min, 20 min and 30 min, respectively, and then cooled in air

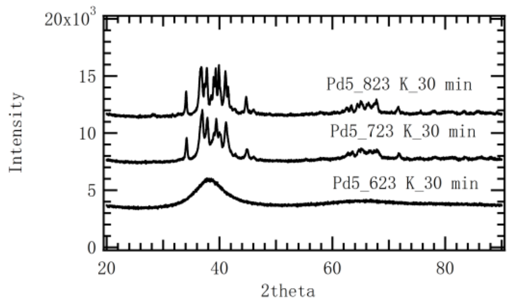
Fig. 3 shows the XRD spectra of the as-cast and annealed $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 2, 5, 15) samples, held at different temperatures (623-923 K) for 30 min and then cooled in air. The as-cast samples of $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 2, 5, 15) showed amorphous structures, indicated by the broad peaks. When the annealing temperature was 623 K(i.e. far below T_g), the amorphous structure remained. When the annealing temperature was 773 K, 823 K or 923 K (i.e. above T_x), crystals appeared, indicated by the sharp diffraction peaks. It suggests that the amorphous-crystalline composite structure was obtained. $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=2, 15) samples annealed at 723 K showed amorphous structures. On the other hand, $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=5) sample annealed at 723 K showed amorphous-crystalline composite structure.



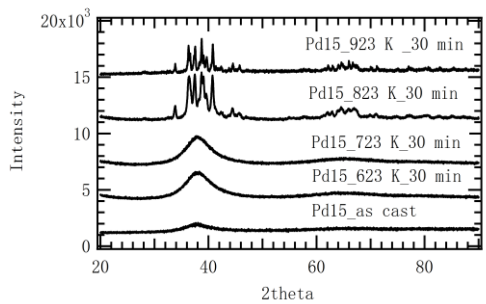
(a)



(b)



(c)



(d)

Fig. 3 XRD spectra of the as-cast and annealed $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 2, 5, 15) samples, held at different temperatures (623-923 K) for 30 min and then cooled in air

Fig. 4 shows the dependence of microhardness on annealing time, held at 823 K for 5 min, 10 min, 20 min and 30 min, respectively, and then cooled in air for $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=5). After annealing for 10 min, the microhardness reached the maximum and then leveled off. The appearance of the crystals lead to the increased microhardness. Fig. 5 shows the dependences of microhardness on annealing temperature for $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 2, 5, 15), held for 30 min and then cooled in air. With increasing annealing temperature, microhardness gradually increased and then leveled off, because crystallinity gradually increased and then reached saturation.

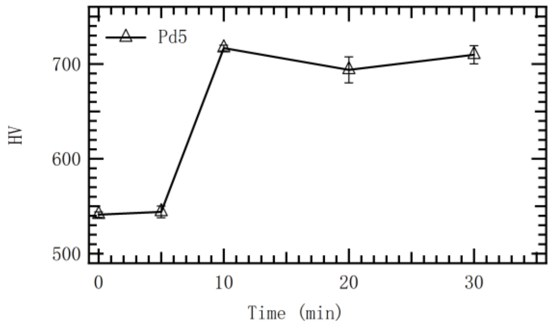


Fig. 4 Dependence of microhardness on annealing time for $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=5), held at 823 K for 5 min, 10 min, 20 min and 30 min, respectively, and then cooled in air

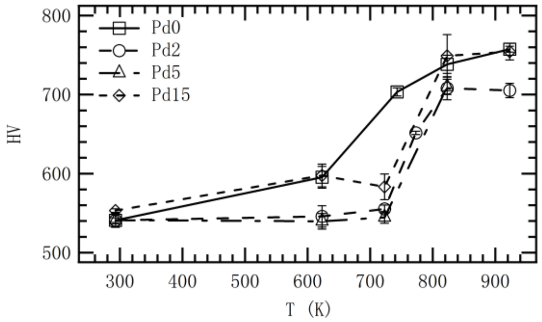


Fig. 5 Dependences of microhardness on annealing temperature for $Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0, 2, 5, 15), held for 30 min and then cooled in air

Conclusions

$Zr_{50}Cu_{40-x}Al_{10}Pd_x$ (x=0-15) BMGs were annealed at different temperatures (below T_g, between T_g and T_x, and above T_x) and for different time period (5 min, 10 min, 20 min, 30 min), and then cooled in air. Annealing temperature and annealing time indicated important effects on the microstructures and microhardness of the samples. According to XRD analysis, the as-cast BMG samples showed amorphous structures. The annealed samples held at 623 K(i.e. far below T_g) for 30 min still showed amorphous structure. The annealed samples held at 773 K, 823 K or 923 K (i.e. above T_x) for 10-30 min showed amorphous-crystalline composite structures. After annealing for 10 min, the microhardness reached the maximum and then leveled off. The increased microhardness was due to the formation of the crystals. With increasing annealing temperature, microhardness gradually increased and then leveled off, because crystallinity gradually increased and then reached saturation. The samples annealed between T_g and T_x may have amorphous or amorphous-crystalline composite structures, depending on the chemical composition.

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