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Pd-Si binary bulk metallic glass

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$Pd_{80+x}Si_{20-x}$ (x = 0, 1, and 2) binary metallic glasses with the diameter ranging from 7 to 8 mm were prepared by a combination of fluxing and water quenching or air cooling. Thermal analysis results show that with increasing Si content, the glass transition temperature T_g, the initial crystallization temperature T_x and the onset crystallization temperature T_p of Pd-Si binary glassy alloys increase. Moreover, the supercooled liquid region reaches 61 K. It indicates that Pd-Si binary alloys possess large glass forming ability, which can be greatly improved by fluxing treatment.

fluxing, bulk metallic glass, binary alloys, glass forming ability, undercooled liquid

Since the first glassy alloy was reported, extensive research has been carried out[1−3]. Amorphous alloy has great potentials for application due to its excellent properties such as high corrosion resistance, low elastic modulus and high strength. However, most of amorphous alloys were prepared in shape of ribbons, thin films or powders by rapid solidification methods ($>1\times10^6$ K/s), which greatly limits their application. So it is very meaningful to develop bulk metallic glasses with three-dimensional size over millimeter. Recently, bulk metallic glasses, such as Pd-Ni-P, Al-La-Ni, Mg-Cu-Y, Mg-Ni-Y, Zr-Al-Ni alloy systems[4−9], were successfully prepared at low cooling rate less than 1000 K/s, which promotes the research and application of amorphous alloys. Furthermore, Inoue proposed three empirical rules for designing and developing bulk metallic glasses based on the obtained experimental results: 1) multi component systems consisting of more than three elements; 2) significant difference in atomic size ratios above about 12% among the three main constituent elements; 3) negative heats of mixing among the three main constituent elements[8,9]. These empirical rules show that the more constituent elements the more difficultly atoms diffuse during the cooling process, and thus the nucleation and crystallization can be depressed, resulting in the increase in the undercooling of alloy melt and the improvement of the glass forming ability. According to these empirical rules, a lot of multicomponent bulk metallic glasses were developed[9−11]. The multicomponents, however, greatly complicate the research on glass forming ability, glass transition and computer simulation. Therefore, it becomes important to develop binary bulk

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metallic glasses. In 2004, several research groups successively developed Cu-Zr binary glassy alloys and the largest size reported was 2 mm[12−14]. Subsequently Pd-Si binary bulk metallic glasses with a diameter of 6 mm were reported to be prepared[15,16]. At the same time the glassy alloys exhibited super deformation ability, with the largest engineering plasticity of about 82% and the corresponding true plasticity of about 170%[17]. Recently, it has been reported that Ni-Nb binary bulk metallic glass was developed with the largest size of 2 mm[18]. These results show that bulk metallic glass can be produced in binary alloy systems. Due to simple constituent elements, binary bulk metallic glass can simplify research on atomic interaction and coordination. Consequently the successful preparation of binary bulk metallic glass has attracted much attention of the researchers.

Our research group has developed $Pd_{81}Si_{19}$ binary bulk metallic glassy ball sample with the largest size of 6 mm in diameter[15], indicating that this alloy possesses large glass forming ability. In this paper, in order to study whether there is other alloy composition near $Pd_{81}Si_{19}$ with large glass forming ability, $Pd_{81+x}Si_{19-x}$ ($x = -2, -1, 0, 1, 2$) binary bulk alloy samples were prepared by using fluxing technology and the microstructures were studied.

1 Experimental procedure

Ingots of the studied $Pd_{81}Si_{19}$ alloy were prepared by melting the mixtures of Pd and Si with over 99.99wt% purities in a high-purity argon atmosphere. $Pd_{81}Si_{19}$ ingots were continuously purified with the fluxing medium B_2O_3 in a quartz tube at about 1423 K. During the purification process, the alloy melt was solidified and remelted several times in order to promote the flux to remove the impurities within the ingots. After purification the alloy samples were prepared by air cooling and water quenching. The cooling rate has been evaluated as 4—8 K/s for air cooling and 40 K/s for water quenching through thermocouple measurement.

The structure of the glassy alloys was examined by X-ray diffractometry (XRD) with monochromatic Cu Kα radiation. The thermal properties of the as-prepared glassy alloy were examined with Shimadzu DSC-60 differential scanning calorimetry (DSC) instrument under the protection of N_2 gas (flow rate: 50 mL/min). The applied heating rates were 10, 20, 40 and 60 K/min. The microstructure of the samples was observed by transmission electron microscope (TEM) using a JEM 200CX (JEOL), a JEM 2011 and a JEM 2010F high resolution transmission electron microscope (HRTEM), operated at 200 kV. The thin foil specimens for TEM observation were prepared by a standard twin-jet electropolishing method. Nano-indentation test was performed at a strain rate of $0.05\ s^{-1}$ by the Nano Indenter indentation instrument with Berkovich tip. Uniaxial compression tests were measured by an Instron testing machine with a strain rate of $3\times10^{-4}\ s^{-1}$. The specimens for the compressive tests ranged from 1 mm × 1 mm × 2 mm to 2 mm × 2 mm × 4 mm or ϕ 3 mm × 6 mm in size, and were cut out from the as-prepared glassy samples.

2 Experimental results and discussion

The XRD patterns of $Pd_{81+x}Si_{19-x}$ ($x = -2, -1, 0, 1, 2$) alloy samples are shown in Figure 1. It is seen that there are sharp diffraction peaks caused by crystalline structure in the XRD spectra of $Pd_{79}Si_{21}$ and $Pd_{83}Si_{17}$ alloys while except the broad diffraction peak, no distinctive sharp diffraction peak can be observed in the XRD spectra of other alloys. The results show that the crystalline phases were formed in $Pd_{79}Si_{21}$ and $Pd_{83}Si_{17}$ alloys while the glassy structure was formed in the other samples. So applying fluxing treatment, $Pd_{80}Si_{20}$ and $Pd_{81}Si_{19}$ glassy ball samples with the diameter up to 8 mm can be prepared, and $Pd_{82}Si_{18}$ glassy ball sample with the diameter of about 7 mm can be prepared, while $Pd_{81}Si_{19}$ glassy rod with the diameter of about 4.6 mm can be produced.

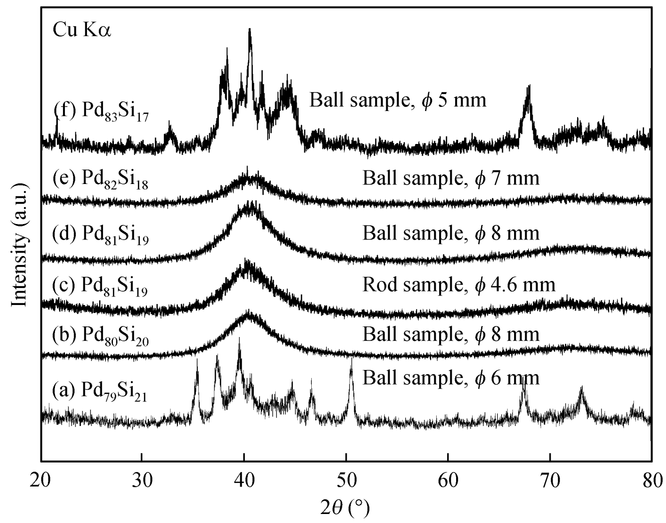

Figure 1 XRD patterns of Pd-Si binary glassy alloys. (a)—(c), (e) and (f) are water quenched samples and (d) is an air cooled ball sample.

Figure 2 shows the high resolution TEM (HRTEM) image of $Pd_{81}Si_{19}$ binary bulk metallic glass, which presents maze-like image. Except for some local ordered atomic arrangement no obvious long range lattice fringe can be found, indicating its amorphous structure. The inset of Figure 2 is the corresponding selected area electron diffraction (SAED). Except for the diffused halos corresponding to the amorphous structure, no distinct evidence of crystalline diffraction spots or thin rings can be found, convincing the amorphous structure of the sample. It agrees well with the XRD result. In addition, lots of structural characteristics of local short (or medium) range order

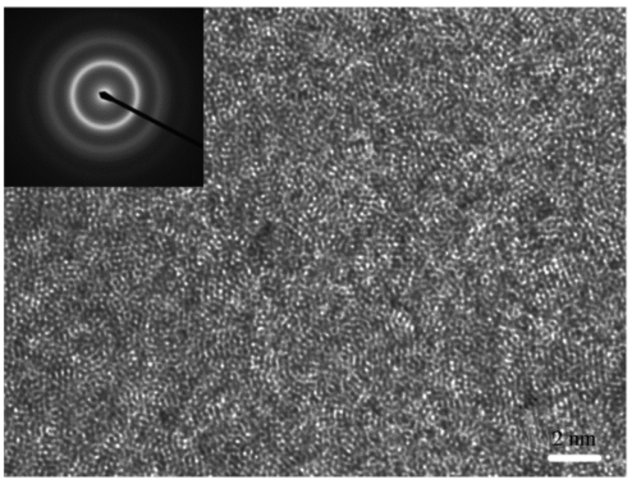

Figure 2 HRTEM image of $Pd_{81}Si_{19}$ binary bulk metallic glass. The inset is the corresponding selected area electron diffraction (SAED) pattern.

can be observed in Figure 2. The details of these local short (or medium) range orders need further study.

Figure 3 shows DSC curves of the prepared glassy alloys, where the glass transition temperature (T_g) and initial crystallization temperature (T_x) as well as the onset crystallization temperature (T_p) are marked with arrows, respectively. It is seen that there are an endothermic reaction and an exothermic reaction during the heating process, respectively. The thermal analysis results have shown that the glass transition temperature T_g of the water quenched $Pd_{80}Si_{20}$ glassy ball (ϕ 8 mm), air cooled $Pd_{81}Si_{19}$ glassy ball (ϕ 8 mm) and water quenched $Pd_{82}Si_{18}$ glassy ball (ϕ 7 mm) is 641, 634 and 630 K, their initial crystallization temperature T_x is 700, 695 and 687 K, and therefore the supercooled liquid region ΔT defined by the difference between T_g and T_x ($\Delta T = T_x - T_g$) is calculated to be 59, 61 and 57 K, respectively. It shows that Pd-Si alloys not only possess large glass forming ability but good thermal stability. The crystallization temperature T_p of the three alloys is 704, 700 and 692 K, respectively, and each alloy exhibits only one crystallization peak, which deviates from the reported result[16]. The reason is not clear at present, but the chemical composition analysis shows that the prepared glassy alloys are binary alloys. According to the above thermal parameters, it is known that with increasing Si content, T_g, T_x and T_p all move to high temperature, indicating the thermal stability of the glassy structure is increased. However, the supercooled liquid region of $Pd_{81}Si_{19}$ glassy alloy is the largest, showing this composition might be the optimal glass forming composition[9−11]. DSC curves of the three glassy alloys all show one strong exothermic crystallization peak, consistent with the compositions near the eutectic point ($Pd_{82.8}Si_{17.2}$).

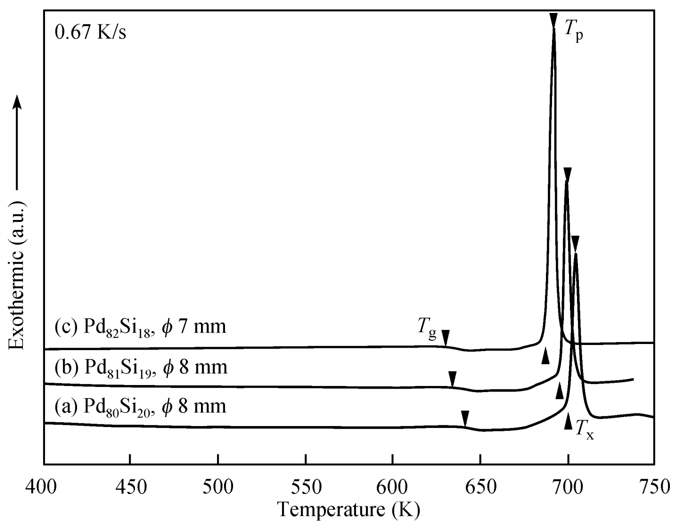

Figure 3 DSC curves of Pd-Si binary bulk metallic glasses. (a) Water quenched $Pd_{80}Si_{20}$ glassy ball; (b) air cooled $Pd_{81}Si_{19}$ glassy ball; (c) water quenched $Pd_{82}Si_{20}$ glassy ball.

The load-displacement *p-h* curve of the nanoindentation test for air cooled $Pd_{81}Si_{19}$ glassy ball is shown in Figure 4. There are a few small discrete pop-in events observed during the load process as the arrows show. The phenomena were also observed in nanoindentation tests of many glassy alloys, such as Zr-based, Ni-based and other metallic amorphous alloys[19−22]. The inset (a) in Figure 4 is a typical nanoindentation with many piling-ups around the indenter, usually observed in metallic glass. Simultaneously, with the indenter falling, the part around the indenter was squeezed and strengthened, and sinking-in was formed[23], more pronounced for strain-hardening materials. The inset (b) is the enlarged image of sinking-in, identifying that strain hardening might occur in this metallic glass during the deforming process. The uniaxial compression test shows that the glassy alloy actually presents super deformation ability and strain hardening phenomenon[17]. The other Pd-Si binary bulk metallic glasses also show super deformation ability and the related results will be reported in another paper.

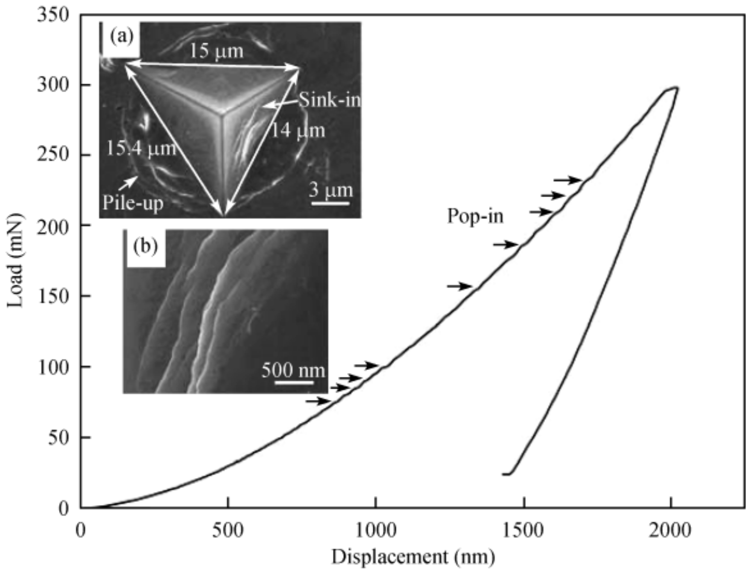

Figure 4 Nanoindentation load-displacement curve of $Pd_{81}Si_{19}$ glassy alloy with the inset (a) SEM of indentation and (b) the enlargement of sinking-in.

How to evaluate glass forming ability (GFA) of alloys has been always a problem that researchers concern. At the present time there are quite a few criteria, among which the most widely used criteria are the reduced glass transition temperature T_{rg}, defined as $T_{rg} = T_g/T_l$, proposed by Spaepen and Turnbull[2]; the supercooled liquid region ΔT advocated by Inoue et al.[8,9]; and the parameter γ, defined as $\gamma = T_x/(T_g+T_l)$, proposed by Lu et al.[24]. The liquidus temperature T_l of $Pd_{82}Si_{18}$, $Pd_{81}Si_{19}$ and $Pd_{80}Si_{20}$ alloys is 1088, 1128 and 1228 K, respectively, and therefore the calculated T_{rg} values are 0.579, 0.562 and 0.522; ΔT of the three alloys are 57, 61 and 59 K, and γ values are calculated to be 0.400, 0.394 and 0.374. These values lie in the range of good glass formers[9−11,24], showing their large glass forming ability. Moreover, $Pd_{82}Si_{18}$ and $Pd_{81}Si_{19}$ alloys with lower Si content might possess larger glass forming ability. However Pd is a kind of noble metals. So it is difficult to carry out a lot of experimental research for using the critical size criterion to evaluate glass forming ability of Pd-Si alloys. From the above results, both T_{rg} and γ values show that Pd-Si binary alloy possesses large glass forming ability.

Pd-Si binary alloy exhibits large glass forming ability and can be produced in bulk metallic glass with a size of 7—8 mm, much larger than the reported binary bulk metallic glasses. It needs further research to determine whether $Pd_{79}Si_{21}$ and $Pd_{83}Si_{17}$ BMGs can be prepared. The present results show that it is difficult to produce $Pd_{79}Si_{21}$ and $Pd_{83}Si_{17}$ BMGs even with a diameter of 5—6 mm.

It is the key factor for the alloy melt to depress the nucleation and growth of crystalline phase and obtain large undercooling degree to form glassy structure during the preparation of glassy alloys[9]. In designing and developing bulk metallic glasses, the addition of multicomponent metals, metalloid or other elements is usually used to inhibit crystallization. Thus, most of the prepared bulk metallic glasses include more than three constituent elements. Therefore, Inoue et al. advocated the empirical rule that more than three constituent elements are necessary in developing bulk metallic glass. In addition to multicomponent addition, fluxing treatment and other technologies are used to remove heterogeneity and suppress the crystallization[25]. In this paper, fluxing technology was used to greatly remove the heterogeneity of Pd-Si alloys. The thermal stability of alloy melt was remarkably improved and the propensity to crystallization was depressed, resulting in the enhancement of undercooling. As a result, the critical cooling rate was largely reduced and the glass forming ability was greatly improved[26−28]. So Pd-Si binary bulk metallic glass can be produced at a very low cooling rate. Moreover, it has been reported that there exists an immiscible gap region under the larger undercooling degree near the eutectic composition in the Pd-Si binary alloy system[29]. Liquid phase separation would take place if the alloy melt stayed at this region for suitable time[30,31], which could reduce the free energy of the system, enable the alloy melt to be metastable and influence the glass forming ability of the alloy. Certainly this problem needs further research.

Due to simple constituent elements of binary bulk metallic glass it is favorable to carry out basic researches relating to metallic glasses. Especially Pd-Si binary bulk metallic glass exhibits a large supercooled liquid region, which enables research on structural relaxation at high temperature and on glass transition. So present results have provided an idea material for studying the basic scientific problems in condensed-matter physics, such as glass transition and glass forming ability. Especially, it would benefit the research of computer simulation.

3 Conclusions

$Pd_{82}Si_{18}$, $Pd_{81}Si_{19}$ and $Pd_{80}Si_{20}$ binary glassy alloys were prepared by using a combination method of fluxing and water quenching or air cooling. The glassy balls were up to 7−8 mm in diameter and the rod samples were about 4.6 mm in diameter. The thermal analysis shows that the largest supercooled liquid region of Pd-Si binary glassy alloys can reach 61 K, indicating that the alloys possess good thermal stability. The large values of the reduced glass transition temperature, the supercooled liquid region and χ parameter show that Pd-Si binary bulk metallic glass possesses large glass forming ability. With decreasing Si content, the glass forming ability of Pd-Si alloys increases. Simultaneously fluxing technology can greatly improve the glass forming ability of Pd-Si alloys. Due to simple constituent elements Pd-Si alloys might be an ideal material for the study on basic scientific problems of bulk metallic glass.

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