Research Article

Formation and Mechanical Properties of Pd-Si Binary Bulk Metallic Glasses

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Glassy spherical samples in the diameters up to 10 mm were produced in a binary Pd-Si alloy system. These Pd-Si bulk metallic glasses (BMGs) combine high strength of about 1600 MPa and superplasticity of over 70% together. In addition to abundant micrometer-scale shear bands, 10–20 nanometer-sized shear bands were also observed on the side surface of the deformed sample. The excellent ductility shown by the Pd-Si BMGs is suggested to arise from the nanoscale structural inhomogeneity.

1. Introduction

The formation of the first metallic glass (MG) in a binary Au-Si system has spurred intensive interest in the fundamental understanding of glass formation and structure-property relationship [1–5]. In particular, the unique mechanical response of bulk metallic glasses (BMGs) makes them more attractive in certain application fields than their crystalline counterparts [6–10]. Based on a “confusion principle,” BMGs are usually formed in multicomponent alloy systems [2–4]. However, some binary alloy systems such as Cu-Zr, Pd-Si, and Cu-Hf as well as Ni-Nb alloys exhibit exceptionally high glass-forming ability (GFA) so that BMGs can be produced from these alloys [11–15]. In addition, these binary BMGs show a combination of both high strength and large ductility [8, 9]. Due to their simple compositions, the binary alloys are more prone to crystallization than the multicomponent alloys, posing extreme difficulties in producing BMGs with sizes larger than 2 mm [11–14]. In this paper, Pd-Si BMGs in the diameter up to 10 mm were produced, which are the largest binary BMGs reported so far. On the basis of the nanoindentation and uniaxial compression tests, the mechanical properties of Pd₈₁Si₁₉ BMG alloys have been studied.

2. Experimental Procedure

Ingots of Pd₈₁Si₁₉ alloys were prepared by melting the mixtures of Pd and Si with over 99.99 wt% purities in an argon

atmosphere. Pd₈₁Si₁₉ ingots were continuously purified by the fluxing medium including B₂O₃ in a quartz tube located in a stove with a constant temperature of 1423 K till glassy alloys were obtained. During this process, the quartz tube was taken out of the stove and cooled under air every 30 minutes in order to promote the fluxing effect. The structure of the glassy alloys was examined by X-ray diffractometry (XRD) with monochromatic CuK_α radiation. The elastic moduli of the Pd₈₁Si₁₉ BMGs, such as Young's modulus and the shear modulus, were obtained by the ultrasonic measurements. The microstructure of the samples was observed by transmission electron microscope (TEM) using a JEM 120EX (JEOL) and a JEM 2010F high resolution transmission electron microscope (HRTEM) with an accelerating voltage of 200 KV. The thin foil specimens for TEM observation were prepared by a standard twin-jet electropolishing method. Nanoindentation tests were performed at a strain rate of 0.5 s⁻¹ by the Nano Indenter indentation instrument of MTS with Berkovich tip. Uniaxial compression tests were measured by an Instron testing machine.

3. Results and Discussions

Figure 1 shows the XRD patterns of Pd-Si binary alloys. The diameter of the spherical Pd₈₁Si₁₉ sample is about 10 mm while the diameter of the Pd₈₀Si₂₀ glassy ball is around 8 mm. Except the broad diffraction peaks, no distinctive sharp diffraction peak resulted by crystalline phases can be

FIGURE 1: XRD patterns of Pd-Si alloys: (a) $\text{Pd}_{81}\text{Si}_{19}$ BMG with a diameter up to 10 mm and (b) $\text{Pd}_{80}\text{Si}_{20}$ BMG with a diameter up to 8 mm.

FIGURE 2: DSC curve of the $\text{Pd}_{81}\text{Si}_{19}$ BMG with a diameter of 10 mm.

observed, indicating that glassy structure was formed in both samples.

Figure 2 presents the DSC curve of the $\text{Pd}_{81}\text{Si}_{19}$ BMG with the near eutectic composition ($\text{Pd}_{82.8}\text{Si}_{17.2}$). The glass transition temperature (T_g), initial crystallization temperature (T_x), and the peak crystallization temperature (T_p) are determined to be 629 K, 691 K, and 693 K, respectively. Thus, the supercooled liquid region ΔT defined by the difference between T_g and T_x ($\Delta T = T_x - T_g$) can be obtained to be as large as 62 K. Meanwhile, the DSC trace shows one distinct exothermic peak corresponding to the subsequent devitrification starting at T_x .

Figure 3 shows the structure of the $\text{Pd}_{81}\text{Si}_{19}$ BMG, which is typical for amorphous materials. No distinct evidence of crystalline diffraction spots or thin rings can be found in the selected-area electron diffraction (SAED) pattern shown in Figure 3(b). This further confirms the samples' amorphous structure. The high resolution transmission electron microscope (HRTEM) image evidences the structural inhomogeneity of the $\text{Pd}_{81}\text{Si}_{19}$ BMGs as shown in Figure 3(c).

FIGURE 3: The microstructure of the $\text{Pd}_{81}\text{Si}_{19}$ BMG: (a) a bright field (BF) image, (b) a selected-area electron diffraction (SAED) pattern, and (c) a HRTEM image.

FIGURE 4: Nanoindentation load-displacement curve of the $\text{Pd}_{81}\text{Si}_{19}$ BMG with the inset: (a) SEM of indentation and (b) the enlargement of sinking-in.

For instance, the medium-range order (MRO) clusters less than 2 nm are frequently observed as indicated by the black circles, corresponding to the outer diffraction ring marked with white arrows shown in Figure 3(b).

Figure 4 shows the load-displacement p - h curve of the nanoindentation test for the $\text{Pd}_{81}\text{Si}_{19}$ BMG at a strain rate of 0.05 s^{-1} . A few small discrete pop-in events can be observed during the load process, indicating the operation of individual shear bands as reported in Zr-based, Ni-based, and other amorphous alloys [16–18]. The piling-up is observed as shown in the upper inset of Figure 4(a). Strikingly, the sinking-in phenomena also appear near the indenter, which are more pronounced for the strain-hardening or the non-strain-hardening materials with a low value of E/Y (where E is elastic modulus and Y is the yielding strength) shown in Figure 4(b) [19]. By using the ultrasonic measurements, the elastic moduli of Young's modulus, the shear modulus, and Poisson's ratio were obtained to be 94.53 GPa, 33.43 GPa, and 0.414, respectively. The yielding strength is about 1600 MPa estimated from the compression test. Then the E/Y can be calculated to be 59, a relatively low value compared

FIGURE 5: The compressive stress-strain curve of the $\text{Pd}_{81}\text{Si}_{19}$ BMG deformed at room temperature.

FIGURE 6: SEM side-view images of a deformed $\text{Pd}_{81}\text{Si}_{19}$ BMG specimen with a plastic engineering strain over 70% (a) $\times 2$ K, (b) $\times 20$ K, (c) $\times 100$ K, (d) $\times 50$ K, and (e) $\times 1000$ K.

with the corresponding crystalline materials. MGs usually show higher yielding strength and lower elastic modulus compared with their crystalline counterparts, leading to relatively low values of E/Y . MGs are thus expected to exhibit the sinking-in phenomena. However, most of the studies on the nanoindentation behaviors of MGs scarcely reported the presence of the sinking-in phenomena [16–18].

Figure 5 shows the compression curve of the $\text{Pd}_{81}\text{Si}_{19}$ BMG, showing a unique combination of a high strength of about 1600 MPa and a large plasticity of over 70%. The SEM side-view images of the compression specimen at a plastic engineering strain of $\sim 70\%$ are shown in Figure 6(a). Different from most monolithic BMGs usually undergoing inhomogeneous plasticity and exhibiting poor ductility

(<1%) at room temperature, quite uniform multiple shear bands are observed with an interspace ranging from 1 to $10\ \mu\text{m}$. Moreover, these shear bands branch and intersect as marked with white arrows. Meanwhile, many small steps of about 50–100 nm in size are formed along the shear bands (see Figures 6(a) and 6(b)). This indicates that the propagation of shear bands could be blocked, resulting in deflection, bifurcation, and branching. The macroscopic morphology of twisted shear bands is thus rough-and-tumble. In addition, the shear bands can be mainly divided into two types marked with black arrows shown in Figure 6(a): A type at an orientation of $\sim 70^\circ$ with respect to the compression direction and B type nearly parallel to the compression direction. Many A type shear

bands are with angles of 35° ~ 50° to the loading axis. It is accepted that the macroscopic plasticity arises from the accumulation of local shear deformation originating from individual shear bands. So the total ductility increases with increasing the number of shear bands [20]. At a higher magnification image shown in Figure 6(b), voids marked by white arrows can be seen. Moreover, the initiation and propagation of the crack are also observed as marked by black arrows in Figure 6(b). Liu and coworkers reported that the formation of voids and cracks was induced by the tensile stress arising from the dilation and coalescence of the free volume [21]. The crack does not propagate along the shear bands but is hindered by the intersecting shear bands as shown in Figure 6(c). However, the intersecting shear bands pile up in Figure 6(d), exhibiting a softening behavior accompanied by microvoids formation.

The high resolution SEM image shows the morphology of microshear bands appearing between the main shear bands shown in Figure 6(e). Many kinks, deflection, and ledges marked by black arrows can be found along the shear bands. The heights of the ledges or kinks are about 10 nm or less. The interspace of these nanoscale shear bands is about 30–50 nm. As indicated by the white arrows in Figure 6(e), the propagation of microshear bands can be locally arrested and the induced new shear bands can be observed ahead.

The nanoscale structural inhomogeneity in $\text{Pd}_{81}\text{Si}_{19}$ is suggested to account for its large plasticity. These MRO clusters could function as a reinforcing source to effectively hinder the further propagation of the matured shear bands and promote formation of new shear bands [22, 23]. Cao et al. also reported that strain hardening occurred in Cu-Zr-Ti metallic glass due to phase separation-induced inhomogeneity during the cold rolling process [24]. This also indicates that the structural inhomogeneity could help generate multiple shear bands contributing to large plasticity. Thus, designing a glass-forming alloy with nanoscale structural inhomogeneity could endow this alloy with a unique combination of high strength and large ductility.

4. Conclusion

$\text{Pd}_{81}\text{Si}_{19}$ binary BMGs were prepared in shape of spheres with diameters up to 10 mm. The supercooled liquid region ΔT of the $\text{Pd}_{81}\text{Si}_{19}$ BMG is 62 K, indicating that the $\text{Pd}_{81}\text{Si}_{19}$ alloys possess high thermal stability and good glass-forming ability. Both piling-up and sinking-in phenomena occurred during the nanoindentation tests, demonstrating a possible strain-hardening deformation mechanism. The uniaxial compression tests proved that $\text{Pd}_{81}\text{Si}_{19}$ glassy alloys exhibit the superductility with a compressive plastic strain over 70%. Abundant shear bands were formed during deforming process, which is attributed to the intrinsically structural inhomogeneity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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