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Effects of the Cooling Rate on the Plasticity of $Pd_{40.5}Ni_{40.5}P_{19}$ Bulk Metallic Glasses *

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We prepare $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples with purified ingots by copper mold casting at a high cooling rate and by water quenching at a low cooling rate. Both of them exhibit different supercooled liquid regions and multiple glass transition characteristics in their differential scanning calorimetric curves. The plasticity of the glassy sample prepared by copper mold casting is about 5% while that prepared by water quenching is almost zero (0.2%), indicating that cooling rate has influenced the plasticity of glassy alloys. By using high resolution TEM image analysis, it is revealed that there exist characteristic regions with different contrasts in the full glassy samples. The characteristic size is about 20–40 nm for the glassy sample prepared by water quenching and 2–4 nm for the one prepared by copper mold casting. The large difference in the plasticity of the glassy samples prepared by different cooling rates is believed to be related to the difference in the size of the characteristic nanoscale structures. The results indicate that adjusting cooling rate in preparation of glassy samples could modify the thermal and mechanical properties of the glassy alloys.

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Bulk metallic glass (BMG) is a kind of new structural and functional material developed in recent years. Because of many excellent demonstrated properties such as high strength, corrosion resistance, elastic deformability and magnetic properties, BMGs have become a hot research topic in the materials field. A large number of BMG alloy systems have been developed and some breakthroughs have been achieved in their mechanical and functional properties.[1–5] The first reported bulk metallic glass with a critical size over one centimeter is the $Pd_{40}Ni_{40}P_{20}$ glassy alloy, which nowadays can be obtained to be as large as 25 mm in diameter.[6] Although $Pd_{40}Ni_{40}P_{20}$ glassy alloy shows a large glass forming ability, it is very brittle with barely global plasticity. Recently, it was found that the bulk glassy alloy system containing precious metal will exhibit large plasticity such as Pd-Si, Pd-Cu-Si and Pt-Cu-Ni-P BMG.[7–11] It has also been found that all of these BMGs with large plasticity possess large Poisson's ratio (γ),[11] which is believed to contribute to the large plasticity of the glassy alloys. $Pd_{40.5}Ni_{40.5}P_{19}$ BMG also exhibits large Poisson's ratio (0.41),[6] suggesting that there might be a way to enhance the plasticity of $Pd_{40.5}Ni_{40.5}P_{19}$ BMG.

Besides composition, cooling rates during solidification could also dramatically change the mechanical property, thermo property and microstructure of both crystalline alloys and glassy alloys.[12–16] In this study, $Pd_{40.5}Ni_{40.5}P_{19}$ bulk glassy samples have been prepared by different cooling rates during solidification. The effect of cooling rate on the thermal and mechanical property of the glassy alloys has also been studied.

$Pd_{40.5}Ni_{40.5}P_{19}$ alloys were prepared by melting the mixture of high purity Pd (99.9%), Ni (99.9%) plates and Ni_2P (99.95%) powder under the protection of high-purity argon gas. To reduce the heterogeneity nucleus as well as improve the stability of the alloy liquid, the $Pd_{40.5}Ni_{40.5}P_{19}$ ingots were then purified by the fluxing medium B_2O_3 in quartz tubes at the temperature of 1423 K in vacuum (3×10^{-3} Pa). The time for purification is about 6–10 h. Finally, the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples with a diameter of 2 mm were solidified at different cooling rates by two methods, water quenching and copper mould casting with the purified ingots, respectively. The cooling rate of water quenching is about 60 K/s (low cooling rate) and the cooling rate of copper mould casting is more than 400 K/s (high cooling rate). The samples for the transmission electron microscope (TEM) were prepared by Twin-Jet polishing technique after mechanical-thinning. The electrolyte is 23vol% perchloric acid and 77vol% glacial acetic acid.

The structures of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples were examined by x-ray diffraction (XRD) analysis using a Japan Rigaku D/max-RB XRD spectrometer with Cu $K\alpha$ radiation. The high-resolution transmission electron microscope (HRTEM) (JOEL-2011) was used to examine the microstructure of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples. The thermal properties of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy alloys were measured by Shimadzu DSC-60 differential scanning calorime-

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try (DSC) instrument under the protection of N_2 gas (flow rate 50 mL/min), which was calibrated with In and Zn standard specimens. Room temperature compression tests of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples were carried out on WDW-100 testing machine at a stain rate of $2.5 \times 10^{-4}s^{-1}$. The cylindrical $Pd_{40.5}Ni_{40.5}P_{19}$ sample for compression test was 4 mm in length and 2 mm in diameter. The fractured surfaces of the $Pd_{40.5}Ni_{40.5}P_{19}$ samples were examined by a QUANTA 200 FEG scanning electron microscope (SEM).

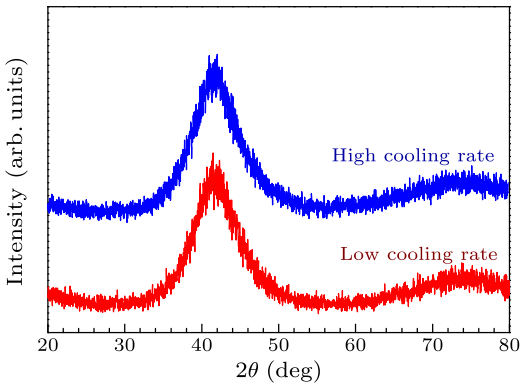


Fig. 1. XRD spectra of the BMGs prepared by water quenching at low cooling rate and copper mold casting at high cooling rate.

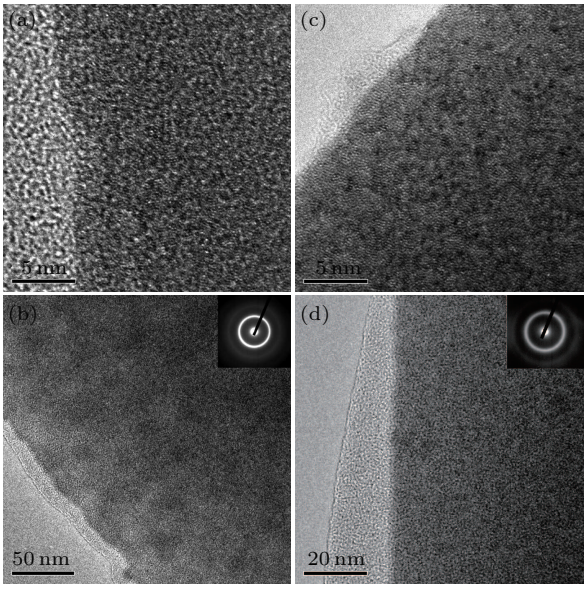


Fig. 2. HRTEM images and bright field TEM images of the BMGs prepared by water quenching at the low cooling rate [(a) and (b)] and copper mold casting at the high cooling rate [(c) and (d)]. Insets: the corresponding SAED patterns.

Figure 1 shows the XRD spectra of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples prepared by two different methods therefore different cooling rates. No sharp diffraction peak could be observed on Fig. 1 except two broad peaks sitting at $2\theta = 42°$ and $2\theta = 74°$ for each spectrum. The XRD results indicate each $Pd_{40.5}Ni_{40.5}P_{19}$ sample solidified at different cooling rate has a glassy phase without signified crystallites. The full width at half maximum (FWHM) of the two $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples was obtained by fitting with a Gaussian function. The FWHM of the peak at 42° for the sample fabricated by water quenching method at low cooling rates is 5.74°, while the FWHM of peak at 42° for the sample fabricated by copper mould casting at high cooling rates is 5.82°. Since the FWHM of a peak in the XRD spectrum is an indicator of the structure disordering, the difference of the FWHM for the two XRD spectra suggests the microstructure of the copper mould casted sample at high cooling rate is more disordered.

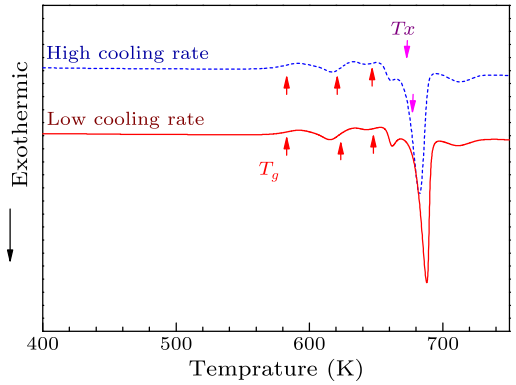


Fig. 3. DSC curves of the BMGs prepared by water quenching at the low cooling rate and copper mold casting at the high cooling rate (20 K/min).

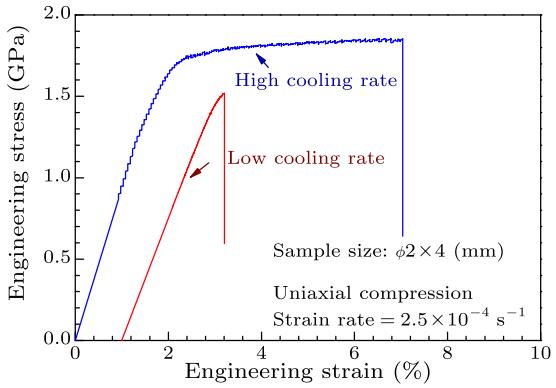


Fig. 4. Stress-strain compression curves of the BMGs prepared by water quenching at the low cooling rate and copper mold casting at the high cooling rate.

The microstructures of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples were examined by TEM. For the sample obtained by water quenching method at low cooling rate, the mass-thickness contrast could be observed on Fig. 2(b). The scope of the dark area in the contrast variation region on Fig. 2(b) is about 20–40 nm in width. The mass-thickness contrast implies that the element distribution is not homogeneous, which might be a result of liquid phase separation during the cooling process. In Figs. 2(c) and 2(d), for the sample

obtained at high cooling rate, the scope of the dark area in the contrast variation region is about 2–4 nm wide, suggesting a smaller characteristic size of the contrast variation region. The corresponding selected area electron diffraction (SAED) patterns are inserted in Fig. 2(b) and 2(d). Except diffused diffraction rings, no sharp diffraction ring or spot could be noticed in the SAED patterns. It is confirmed that the samples prepared at different cooling rates are of fully glassy structure, which is consistent with our XRD results.

Figure 3 presents the DSC curves of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples prepared by two different methods. The DSC heating rate is set to 20 K/min. It could be seen that both the water quenched sample and the copper mould casted sample exhibit three glass transition temperatures, suggesting that both the glassy alloys have experienced a phase separation during cooling process. For the copper mould casted sample at high cooling rates, the onset glassy transition temperature T_g is 570 K, the onset crystallization temperature T_x is 670 K and, therefore, the supercooled liquid region ΔT ($\Delta T = T_x$-T_g) is 100 K. For the water quenched sample at low cooling rate, T_g is 571 K, T_x is 678 K and ΔT is 107 K.

Table 1. Thermal dynamic parameters of the BMG alloys prepared by water quenching at the low cooling rate and copper mold casting at the high cooling rate (20 K/min).

	T_g (K)	T_x (K)	ΔT (K)	T_p (K)
Low cooling rate sample	571/618/646	678	107	688
High cooling rate sample	570/619/644	670	100	682

Table 1 lists the thermal parameters of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples prepared by the two different cooling rates. Note that the sample solidified at the low cooling rate shows a larger supercooled liquid region.

Figure 4 shows the room-temperature compressive stress-strain curve of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples prepared by the two different cooling rates. For the sample obtained at the low cooling rate, the yield strength is 1.51 GPa and the plastic deformation is 0.2%. For the sample obtained at high cooling rate, the yield strength is 1.64 GPa which is 139 MPa higher than the sample obtained at low cooling rate and the plastic strain is increased up to 5%. It is known that when the cooling rate is higher, more free volume, which might serve as the activation sites for shear bands, would be frozen in the glassy alloy.[17,18] Then, activation of multiple shear bands would be promoted, resulting in enhancement of compressive plasticity.[17,18] Usually, the specimen with more free volume concentration resulted by higher cooling rate exhibits lower yielding strength due to the looser atomic structure.[15] However, as shown in Fig. 4, the yielding stress for the specimen prepared by higher cooling rate is higher than that prepared by low cooling rate. According to Fig. 2 and Table 1, the glassy samples prepared with different cooling rates possess similar T_g. This implies that the effects resulted from difference in glass transition temperature can be ruled out.[18] We believe that higher strength for the copper mold casting sample is resulted from the fine local heterogeneous structures induced by liquid phase separation (Fig. 3), since finer local heterogeneous structure may induce more resistance to the activation and propagation of shear bands.

The fractured surfaces of the deformed $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples are examined by SEM. Figure 5(a) shows the fractured surface of the sample obtained at low cooling rate. The river-like pattern could be seen on most parts of the image, which corresponds to the barely plasticity region. Some vein-like patterns among the river-like pattern could also be noticed, which are shear traces part resulted by the local temperature increasing during the compression test. Figure 5(b) shows the fractured surface of the sample obtained at high cooling rate. Compared with the sample obtained at the low cooling rate, there are more areas showing vein-like patterns. Some petal-like patterns that have not been found in the SEM image of the sample obtained at low cooling rate could also be observed here. The results of SEM fractography images for the two samples are also consistent with our previous room temperature compression test that the sample prepared at high cooling rate possesses large plastic deformation ability.

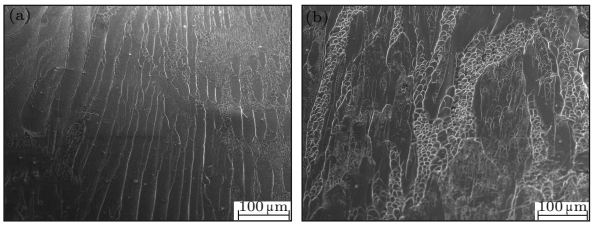


Fig. 5. SEM images of fracture surface for BMGs prepared by water quenching at the low cooling rate (a) and copper mold casting at the high cooling rate (b).

The present result indicates that the mechanical properties, especially the plasticity, of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples prepared at different cooling rate are quite different. The $Pd_{40.5}Ni_{40.5}P_{19}$ bulk glassy samples prepared by copper mold casting at high cooling rate possesses good plasticity, which is greatly larger than that prepared by water quenching at low cooling rate. The difference in plasticity should be related with the difference in the microstructure resulted by the cooling rate. As the cooling rate is increased, the solidification time is reduced. Therefore the diffusion time of atoms is reduced. Based on the DSC results showing in Fig. 3, phase separation might be occurred during the solidification processes of the

$Pd_{40.5}Ni_{40.5}P_{19}$ bulk glassy samples. For the sample prepared at high cooling rate, the time for the developing of the phase separated structure is limited. The atoms do not have enough time to diffuse, resulting in forming a small size phase separated structure,[19,20] consistent with the characteristic regions with different contrast (Fig. 2(b) and 2(d)), which are believed to be a result of phase separation. These regions with different contrasts might have different critical shear stress for activation of shear bands or different resistance for hindering the propagation of shear bands. Then it would promote activation of multiple shear bands and enhance the plasticity of the BMG.[7,20–22] It is found that the sample with 2–4 nm in characteristic size (Figs. 2(c) and 2(d)) exhibits good plasticity. The similar result has also been observed in a Pd-Si BMG, which possesses 3–6 nm nanoscale phase separated structure and exhibits super large plasticity. The reason that the sample with large characteristic size (20–40 nm in size (Fig. 2(b)) is very brittle is still unclear. According to Figs. 4 and 5, it might be related with the crack nucleation in the early deformation stage, which results in premature fracture. To understand the exact reason, more work still needs to be carried out. The present result indicates that the plasticity of BMGs is sensitive to the characteristic size of the chemical or structural inhomogeneity within the glassy alloy. The characteristic size around several nanometers is beneficial to the plasticity of the BMGs.

In summary, it has been found that both of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy samples prepared by water quenching at low cooling rate and by copper mold casting at high cooling rate exhibit multiple glass transition characteristics in their DSC curves, suggesting that they have experienced phase separation during the cooling process. The supercooled liquid region ΔT of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy alloy prepared at the high cooling rate is about 100 K, i.e. 7 K less than that prepared at the low cooling rate ($\Delta T = 107$ K). High resolution TEM image analysis reveals that there exist characteristic regions with different contrasts in the full glassy samples. The characteristic size is about 20–40 nm for the glassy sample prepared by water quenching and 2–4 nm for that prepared by copper mold casting. The plasticity of the $Pd_{40.5}Ni_{40.5}P_{19}$ glassy alloy prepared by copper mold casting at the high cooling rate is about 5%, while that prepared by water quenching at the low cooling rate is only about 0.2%. The present results indicate the cooling rate during solidification process of glassy samples has affected the thermal and mechanical properties of the as-prepared BMGs. The improvement on the plasticity of the glassy alloy by enhanced cooling rate is believed to be related to the nanometer scale characteristic structure resulted from phase separation during solidification. The higher cooling rate would induce a larger frozen-in free volume, which might be another reason for the plasticity enhancement. However, the exact reason for the improvement of mechanical properties of the glassy alloys is still not fully understood.

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