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Influence of flux treatment on the glass forming ability of Pd-Si binary alloys

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Abstract: $Pd_{81}Si_{19}$ amorphous alloys were prepared by combination methods of melt spinning and B_2O_3 flux treatment. A comparison between the ribbons prepared from the fluxed ingots and the non-fluxed ones has been carried out. The result reveals that after fluxing treatment the glass transition temperature of the as-prepared glassy ribbons is reduced while the initial crystallization temperature is enhanced. It results in that the supercooled liquid region (defined as the difference between the initial crystallization temperature and the glass transition temperature) of the glassy alloy treated with fluxing technology has been increased from 31 to 42 K. This shows that fluxing technique can enhance the glass forming ability (GFA) of the binary alloy and improve the thermal stability of supercooled liquid of the glassy alloy.

Key words: amorphous alloys; flux treatment; glass forming ability; supercooled liquid region

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1. Introduction

Metallic glass has been of great technological and scientific interest since its successful production by using splat-cooling techniques in 1960 [1]. Duwez and his collaborators found that Pd-Si alloys with amorphous structure could be obtained in the composition range of 15at%-23at% Si by splat-cooling [2] and over the past decades intensive efforts have been carried out on this alloy system. However, most of the Pd-Si amorphous alloys were prepared only in shape of thin films and ribbons at very high cooling rates (>10^4 K/s) and the critical cooling rate for this alloy system was estimated to be 1000 K/s [3]. Very recently $Pd_{81}Si_{19}$ bulk metallic glasses (BMGs) with a diameter up to 6 mm were successfully prepared at a cooling rate less than 10 K/s, indicating that this binary alloy system indeed possesses large glass forming ability [4-5]. Thus studying on the reason why the glass forming ability (GFA) of Pd-Si alloys was greatly improved will be very meaningful for providing some guidance for preparing BMGs of other alloy systems.

When a liquid is cooled from the melting point at a certain cooling rate, it either crystallizes or continues cooling in an undercooled liquid state. If crystal nucleation is depressed due to kinetic constraints, the supercooled liquid can eventually be cooled to a temperature, at which the liquid fails to reach equilibrium at experimental time scales and becomes a glass [6]. Kui [7] found that heterogeneous nucleation may be hindered and large undercooling can be achieved in melts held in a molten flux such as B_2O_3. In 1982-1983, using fluxing methods, the Turnbull's group succeeded in obtaining about 1-cm vitrified ingots of a Pd-Ni-P alloy at cooling rates well below 100 K/s [8]. Kui and co-workers formed spheres with about 7 mm in diameter of $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass at a low cooling rate of about 0.75 K/s [9]. Nevertheless, there has been no data on the effect of flux treatment on Pd-Si amorphous alloys.

The study on the formation of amorphous $Pd_{81}Si_{19}$ ribbons prepared by melt spinning both fluxed ingots and non-fluxed ones was reported in this paper. By comparing the two kinds of ribbons, the effect of B_2O_3 flux treatment on glass forming ability was discussed.

2. Experimental procedure

The $Pd_{81}Si_{19}$ ingots were prepared by melting the mixtures of high pure Pd and Si plates (purity higher than 99.99%) under argon atmosphere. Some ribbons were prepared directly by melt spinning some of the

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raw $Pd_{81}Si_{19}$ ingots while the other raw ingots were purified with fluxing technology. At first, B_2O_3 was melt in a quartz tube and kept above 1300 K for more than 2 h in vacuum condition. Then a raw $Pd_{81}Si_{19}$ ingot was immersed in the molten B_2O_3 of vacuum about 10^{-3} Pa. The sample was fluxed for more than 10 h at about 1400 K to facilitate the removal of heterophase impurities. Then the system was cooled down to room temperature in air. Both non-fluxed and fluxed samples were remelted and rapidly solidified on a single copper roller at a surface velocity of 25 m/s. The thickness of both ribbons was ~52 μm. The structure of as-prepared samples was examined by X-ray diffraction (XRD). 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 heating rates used are 10, 20, 40, 60 K/min. The instrument was calibrated with In and Zn standard specimens.

3. Results and discussion

Fig. 1 shows the XRD spectrum of the melt spun ribbons of $Pd_{81}Si_{19}$ alloys. Except the broad diffraction peak, no detectable sharp diffraction peak can be observed in both XRD patterns. Therefore, glassy structure was obtained in both ribbons prepared from fluxed and non-fluxed ingots. The broad diffraction peak located at $2\theta \approx 41°$ has been fitted with computer using Lorentz line profiles. For each spectrum, the full width at half maximum (FWHM) has been carefully measured. Both melt-spun ribbons possess almost the same FWHM value of 5.35°, indicating that the atomic disorder of them is similar.

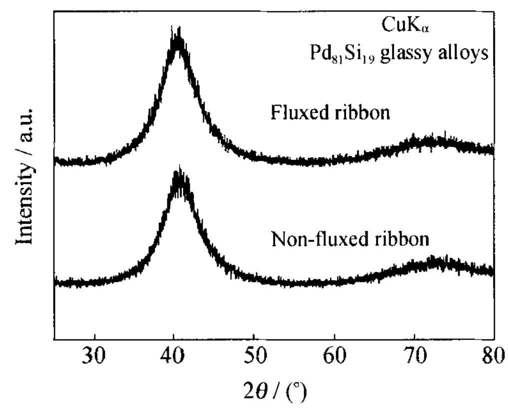

Fig. 1. XRD spectra of $Pd_{81}Si_{19}$ glassy alloys.

When amorphous alloys are heated, the glass undergoes structural relaxation and internal equilibrium is approached. If the glass has transformed to corresponding crystalline phases, some excellent properties will disappear such as good ductile property and high corrosion resistance. Hence high quality amorphous alloys require good thermal stability. From DSC curves given in Fig. 2, it is clear to find that the glass transition temperature T_g reduced from 630 to 627 K and the initial crystallization temperature T_x increased from 661 to 669 K with the onset peak temperature T_p shifting from 678 to 684 K, respectively, thus the supercooled liquid region ΔT of the fluxed ribbons was 42 K, much larger than 31 K of the non-fluxed ribbons, indicating the glassy structure of the fluxed ribbons is more thermodynamically stable.

Comparing ΔT of both ribbons shown in Fig. 2, it can be concluded that it is the fluxing method used in the sample preparing process that leads to a significant increase in the supercooled liquid region. The rise of T_x is due to the removal of impurities, which brings about the reduction of the ease of heterogeneous nucleation and the crystallization suppression. The similar tendency is also recognized for Pd-Ni-P and Pd-Ni-Cu-P, which indicated that the flux treatment is effective for the decrease of critical cooling rate for glass formation through the suppression of the precipitation of a crystalline phase [10]. Since the supercooled liquid region ΔT becomes wider obviously, the thermal stability of the supercooled liquid has been significantly enhanced by fluxing technique.

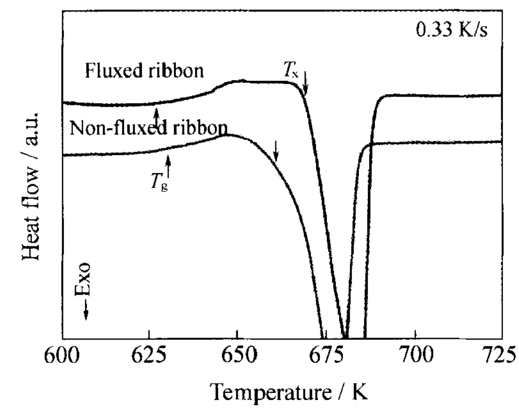

Fig. 2. DSC curves of both fluxed and non-fluxed $Pd_{81}Si_{19}$ glassy ribbons.

The influence of heating rate on the heat flows of the melt spun $Pd_{81}Si_{19}$ glassy alloy *versus* temperature was also examined through DSC measurements by using different heating rates of 10, 20, 40, 60 K/min. The related values are shown in Table 1. As the heating rate increases, it is similar for both ribbons that the corresponding T_g, T_x, T_p and ΔT increase gradually and display a strong dependence on the heating rate, indicating the related transitions are dynamic processes. Chen and Turnbull reported that ΔT of $Pd_{80}Si_{20}$ and $Pd_{82}Si_{18}$ glassy ribbons were 12 and 10 K, respectively [11]. Although ΔT of $Pd_{80}Si_{20}$ ribbons would be evaluated to be about 20 K according to today's determination method of T_g and T_x, the values were still much lower than the fluxed $Pd_{81}Si_{19}$ glassy alloy. Here, the effect of cooling rate on ΔT and amorphous stability should be taken into consideration. The present ribbons with a thickness of ~52 μm were obtained by rapidly solidifying of the melt on a single copper roller at a surface velocity of 25 m/s, which corresponded to the cooling rate of about 10^5 K/s. This cooling rate was one order of magnitude less than that of splat method adopted in Ref. [11]. At the same time, the slight difference in composition is believed to contribute to such large difference between the present ribbons and the reported ones. Thus, it can be concluded that the composition of $Pd_{81}Si_{19}$ might be the best glass former in Pd-Si system, which is near the deep eutectic point and prefers to the steeper side of the binary phase diagram. It agrees with the pinpoint for determining the optimal composition for glass formation in a binary diagram without perfect symmetry [12]. In addition, the deviation of the best glass-forming composition from, but close the eutectic composition was believed to originate from the presence of liquid phase separation reported in Ref. [13].

Table 1. Thermal parameters of the as-prepared $Pd_{81}Si_{19}$ glassy ribbons

Pd81Si19	Heating rate / ($K\cdot min^{-1}$)	T_g / K	T_x / K	T_p / K	ΔT / K	E_p / ($kJ\cdot mol^{-1}$)	E_g / ($kJ\cdot mol^{-1}$)
Fluxing + Melt-spun	10	625	661	675	36	292.9	703.5
	20	627	669	684	42		
	40	629	678	693	49		
	60	632	682	698	50		
Melt-spun	10	628	654	669	26	304.3	547.0
	20	630	661	678	31		
	40	634	671	687	37		
	60	637	678	692	41		
$Pd_{80}Si_{20}$[11]	20	655	667	—	12	—	—
$Pd_{82}Si_{18}$[11]	20	648	658	—	10	—	—

According to Kissinger equation [14]:

$$\ln(\frac{T^2}{\phi}) = \frac{E}{RT} + C,$$

where ϕ is the heating rate applied in DSC measurement, E the apparent activation energy for crystallization, R the gas constant, C the constant.

The Kissinger plots of crystallization of both melt spun ribbons are shown in Fig. 3, where $\ln(T^2/\phi)$ and $1/T$ display a good linear relationship. The apparent activation energy values of crystallization derived from the rates of slope are shown in Table 1. Compared with the non-fluxed ribbons, the apparent activation energy of crystallization for the melt-spun ribbon through flux treatment reduces slightly from 304.3 to 292.9 KJ/mol. The result reveals that the thermal stability of the melt-spun ribbon of fluxed $Pd_{81}Si_{19}$ alloy is much higher.

The reduced glass transition temperature $T_{rg}=T_g/T_l$, proposed by Turnbull, and parameter $\gamma=T_x/(T_g+T_l)$, a new indicator of GFA for bulk metallic glasses proposed by C.T. Liu, are widely used parameters to predict the GFA of alloys [15-16]. For $Pd_{81}Si_{19}$ alloys with liquidus temperature T_l=1140 K, T_g/T_l and γ can be calculated to be 0.550 and 0.379 for the ribbons prepared with the fluxed ingots and 0.553 and 0.373 for non-fluxed ones. Because T_g and T_l are almost invariable for the same alloys, γ is more preferable rather than T_{rg}. Thus, it suggests that the ribbons made by fluxed ingots possess the larger GFA due to a larger γ. At the same time, the value of γ is only a little smaller than those of well-known Vitreloy 1 and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ with large glass forming ability, indicating Pd-Si alloys actually possess large GFA [17].

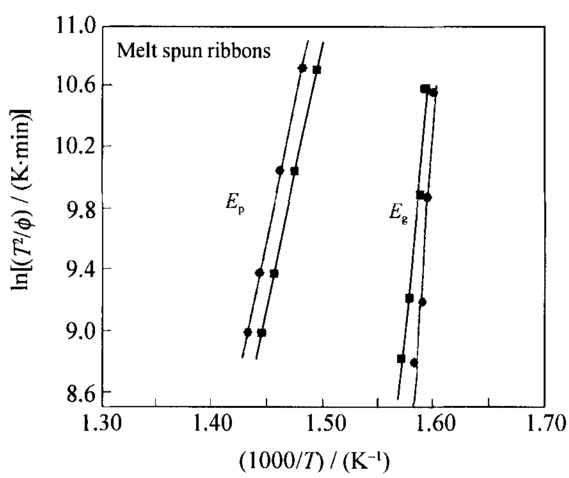

Fig. 3. Kissinger curves of crystallization of the fluxed $Pd_{81}Si_{19}$ ribbons marked with circle and the non-fluxed ones marked with square.

4. Conclusion

The melt-spun $Pd_{81}Si_{19}$ glassy alloy was prepared by combination methods of flux treatment and melt spinning. Thermal analysis shows that the supercooled liquid region ΔT of the glassy ribbons has been increased from 31 to 42 K due to the enhancement of 8 K in the initial crystallization temperature T_x and the reduction of 3 K in the glass transition temperature by fluxing technology. The experimental results show that fluxing technique can enhance the glass-forming ability (GFA) of a Pd-Si binary alloy and improve the thermal stability of supercooled liquid of the glassy alloy.

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