



Thermal stability and fragility of Pd–Si binary bulk metallic glasses

Na Chen, Yang Li, Ke-Fu Yao*

Department of Mechanical Engineering, Tsinghua University, Qinghua Yuan, Haidian District, Beijing 100084, China

ARTICLE INFO

Article history:

Received 31 July 2009

Received in revised form 18 January 2010

Accepted 10 February 2010

Available online 18 February 2010

Keywords:

Metallic glasses

Thermal analysis

Calorimetry

Binary alloy

Fragility

ABSTRACT

The thermal stability of the glassy structure and the supercooled liquids of Pd_{80+x}Si_{20-x} ($x=0, 1, \text{ and } 2$) binary bulk metallic glasses were investigated by differential scanning calorimetry. It is found that Pd–Si binary metallic glasses exhibit large activation energy for glass transition and crystallization, indicating the glassy structure and the supercooled liquids possess high thermal stability. Based on the kinetic nature of the glass transition and thus the resulted heating rate dependence, the fragility index of the Pd–Si binary glassy alloys has been obtained, and compared with other bulk metallic glasses.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Since bulk metallic glasses (BMGs) were developed by the researchers, most of them are constituted by more than three kinds of elements [1–5]. Inoue proposed that a multi-component alloy is most likely to possess large glass forming ability when more than three kinds of constituent elements simultaneously show large different atomic size ratios above 12% and negative heats of mixing [6]. However, Cu–Zr [7–9] binary BMGs were successfully prepared by several groups in 2004, indicating that the binary alloy can also be cast into bulk form with low cooling rates of 10² K/s or less despite of its simple constituents. Thus, BMGs can be divided into two categories in terms of the constituent elements. One is multi-component glass with more than three kinds of constituent elements, the other is binary bulk metallic glass. Many researchers show great interest in binary BMGs and soon a few new binary BMGs were successfully prepared [10–12]. The complexity of multi-component systems is remarkable reduced due to simple interaction between the only two constituent elements, which favors the research on basic theoretical problems regarding glass forming ability and glassy structure.

It is found that a new Pd–Si binary metallic glass [13] exhibits super ductility with an engineering strain over 80%. Nanocrystals toughened Cu–Zr binary metallic glass also shows a large plasticity over 50% [14], indicating that binary BMGs might show more

order glassy structure, resulted by easier atomic diffusion than those conventional multi-component glassy alloys, and thus possess exceptional mechanical properties. So it is meaningful to pay more attention to the formation of binary metallic glasses and research on its properties. It is well accepted that whether a metallic glassy alloy can be prepared into bulk form closely depends on its glass forming ability. However, the glass forming ability of Pd–Si alloy has not been well evaluated. Here, the thermal stability of Pd–Si binary bulk metallic glasses will be studied. In addition, the fragility of Pd–Si binary metallic glass would be used to assess its glass forming ability through comparing to the other good Pd-based glass formers.

2. Experimental procedure

Ingots of the studied Pd_{80+x}Si_{20-x} ($x=0, 1, \text{ and } 2$) alloys were prepared by melting the mixtures of Pd and Si with over 99.99 wt% purities in a high-purity argon atmosphere. Pd–Si ingots were continuously purified with the fluxing medium B₂O₃ for about 10 h 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 spherical alloy samples were prepared by air cooling or water quenching. The structure of the glassy alloys was examined by X-ray diffractometry (XRD) with monochromatic Cu K α 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 N₂ gas (flow rate: 50 ml/min). The heating rates are 5, 10, 20, 30, 40, 60, 80 and 100 K/min, respectively.

3. Experimental results and discussions

The XRD patterns of Pd_{80+x}Si_{20-x} ($x=0, 1, \text{ and } 2$) alloy samples with diameters up to 8 mm are shown in Fig. 1. It is seen that except the broad diffraction peak, no distinctive sharp diffraction peak

* Corresponding author. Tel.: +86 10 62772292; fax: +86 10 62770190.
E-mail address: kfyao@tsinghua.edu.cn (K.-F. Yao).

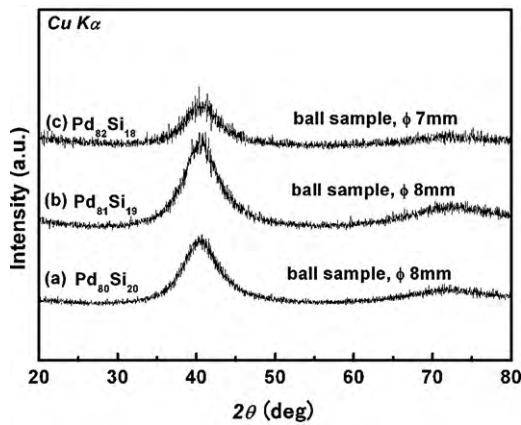


Fig. 1. XRD patterns of $\text{Pd}_{80+x}\text{Si}_{20-x}$ ($x=0, 1, \text{ and } 2$) binary glassy alloys.

resulted by crystalline structure can be observed in the XRD spectra of $\text{Pd}_{80+x}\text{Si}_{20-x}$ ($x=0, 1, \text{ and } 2$) alloys.

In order to investigate the influence of the heating rate on the heat flows, the glass transition and crystallization behaviors as well

as the thermal stability of Pd–Si BMGs, DSC measurements were carried out at the heating rates (ϕ) of 10, 20, 40, 60 and 80 K/min, as shown in Table 1 and Fig. 2. It can be seen that at a heating rate of 20 K/min, the glass transition temperature T_g of the water quenched $\text{Pd}_{80}\text{Si}_{20}$ glassy ball (ϕ 8 mm), air cooled $\text{Pd}_{81}\text{Si}_{19}$ glassy ball (ϕ 8 mm) and water quenched $\text{Pd}_{82}\text{Si}_{18}$ glassy ball (ϕ 7 mm) is 629 K, 629 K and 624 K, the initial crystallization temperature T_x is 692 K, 688 K and 681 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 63 K, 59 K and 57 K, respectively. With increasing heating rate, T_g , T_x and T_p all transform to higher temperature, indicating that they are kinetic parameters, obviously influenced by the heating rates.

According to Kissinger equation [15]:

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

(ϕ : heating rate applied in DSC measurement; E : apparent activation energy for glass transition or crystallization; R : gas constant; C : constant.) The Kissinger's linear relationship between $\ln(T^2/\phi)$ and $1/T$ for the onset temperatures of the glass transition and crystallization is shown in Fig. 2(a)–(c). Thus the activation energy for

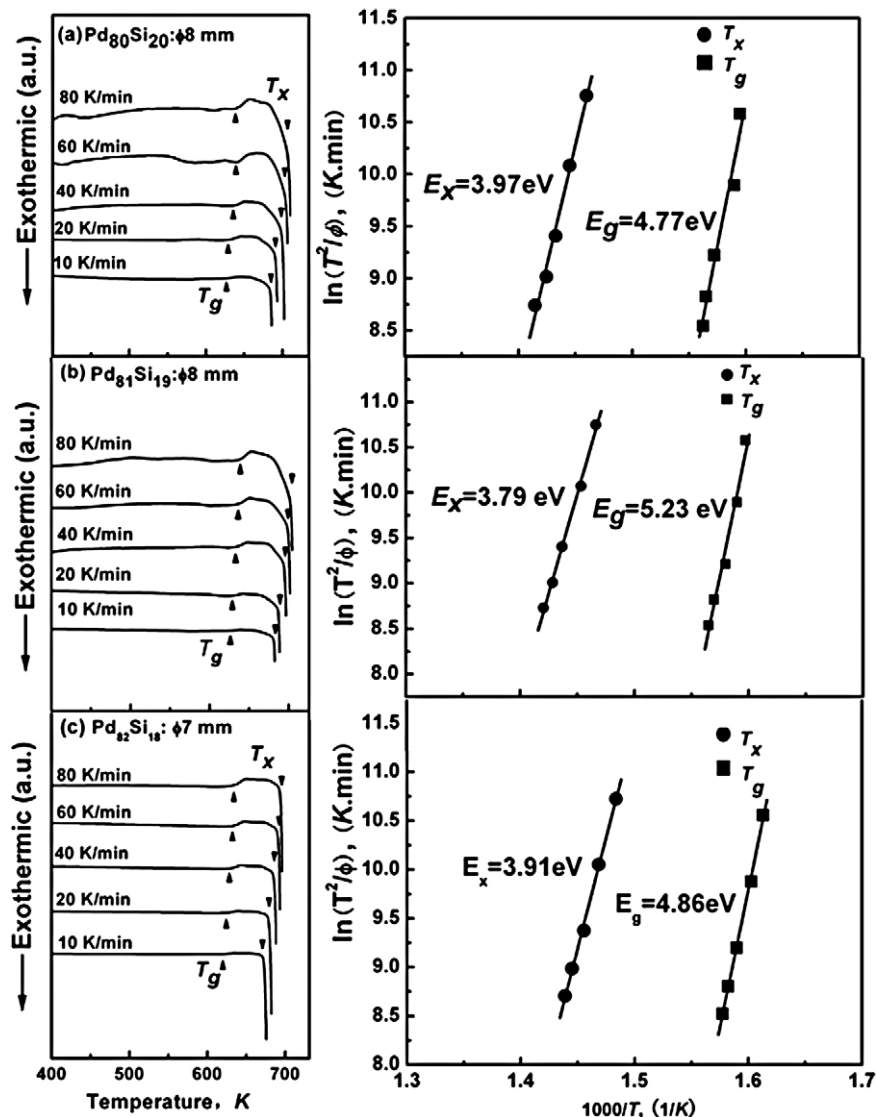


Fig. 2. DSC traces and Kissinger's curves of $\text{Pd}_{80+x}\text{Si}_{20-x}$ ($x=0, 1, \text{ and } 2$) metallic glasses.

Table 1
The activation energy of glass transition (E_g) and crystallizations (E_x) of selected metallic glasses.

Metallic glasses	T_g at different heating rate (K/min)					E_g (eV)	E_x (eV)
	10	20	40	60	80		
Pd ₈₀ Si ₂₀	627	629	636	639	640	4.77	3.97
Pd ₈₁ Si ₁₉	626	629	633	637	639	5.23	3.79
Pd ₈₂ Si ₁₈	620	624	629	632	634	4.86	3.91
Pd ₇₇ Cu ₆ Si ₁₇ [17]						6.56	
Pd ₄₀ Ni ₄₀ P ₂₀ [17]						5.68	
Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀ [17]						6.01	
Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5} [18,19]						5.8	

glass transition (E_g) and crystallizations (E_x) of Pd_{80+x}Si_{20-x} ($x=0, 1$ and 2) glassy alloys can be obtained as about 4.77 eV and 3.97 eV for Pd₈₀Si₂₀, 5.23 eV and 3.79 eV for Pd₈₁Si₁₉, and 4.86 eV and 3.91 eV for Pd₈₂Si₁₈ alloys, respectively (see Table 1). With the variation in Si addition, the values of E_g and E_x show visible difference. It can be concluded that either E_g or E_x is very sensitive to the composition of the alloy. E_g and E_x are important kinetic parameters to evaluate thermal stability of glassy structure and the supercooled liquid, which can be used to investigate the glass transition and crystallization behaviors. The higher the values of E_g and E_x , the better the thermal stability of glassy alloys [16]. The E_g of some other good glass formers is also listed in Table 1. It can be seen that Pd-based metallic glasses possess large values of E_g [17], which is close to that of Zr₄₁Ti₁₄Cu_{12.5}Ni₁₀Be_{22.5} bulk metallic glass (5.8 eV) [18,19], indicating the high thermal stability of their glassy structure. With increasing Si of Pd–Si alloys, E_g increases firstly and then decreases while E_x shows a reverse changing trend. E_g is closely related to the phase transformation from glassy structure to the supercooled liquid. So it reflects the thermal stability of the glassy structure. Compared to Pd₈₀Si₂₀ and Pd₈₂Si₁₈, Pd₈₁Si₁₉ possesses the highest value of E_g , indicating that its glassy structure should be most stable. E_x is prone to give information of the difficulty for the transition from the supercooled liquid to crystallization. It reflects the thermal stability of the supercooled liquid. Pd₈₀Si₂₀ alloy possesses the largest value, showing its highest stability of the supercooled liquid among the three alloys.

Angell introduced the fragility parameter m , defined as the following equation, to assess glass forming ability of supercooled liquids [20–22].

$$m = \frac{D^*}{\ln 10} \times \frac{T_g^0}{T_g} \times \left[\frac{1 - T_g^0}{T_g} \right]^{-2} \quad (1)$$

Here, D^* is the strength parameter, T_g^0 is the asymptotic value of T_g , which is usually approximated as the onset of the glass transition temperature at the limit of infinitely slow cooling and T_g is the glass transition temperature at a heating rate of 20 K/min. The variation of T_g with the heating rate ϕ can be fitted by using Vogel–Fulcher–Tammann (VFT) equation [23]:

$$\ln \phi = \frac{\ln B - D^* T_g^0}{T_g - T_g^0} \quad (2)$$

where B is a constant. Thus, D^* and T_g^0 can be obtained through VFT fits. If applying these values to Eq. (1), the fragility index can be calculated.

Fig. 3 shows the variation of $\ln \phi$ with T_g in an Arrhenius plot for Pd_{80+x}Si_{20-x} ($x=0, 1$ and 2) glassy alloys, respectively. The fragility index m of Pd–Si alloys can be extracted from their VFT fits in Fig. 3, which ranges over 47, 49 and 56 for Pd₈₂Si₁₈, Pd₈₁Si₁₉ and Pd₈₀Si₂₀ glassy alloys (see Table 2). With increasing Si content, the fragility index increases too.

For Pd–Si binary alloys, the eutectic composition is Pd_{82.8}Si_{17.2}, which is closest to Pd₈₂Si₁₈ among these three alloys. It is well

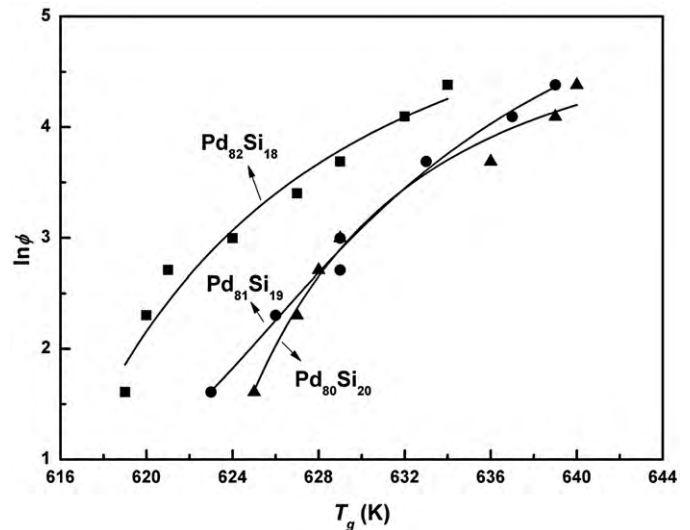


Fig. 3. VFT fits of Pd–Si glassy alloys.

accepted that the eutectic alloy is easier to obtain large undercooling when solidified from high temperature, which renders its supercooled liquid more stable. It indicates a smaller reduction in the transition enthalpy from the supercooled liquid to the solidified glass for Pd₈₂Si₁₈ alloy compared to the other two alloys further off the eutectic composition. So the nearer to the eutectic one the alloy is, the stronger the liquid is. It indicates that the fragility index agrees with that the deep eutectic alloys always present larger glass forming ability. According to the concept of fragility, glass forming liquids can be classified into three general categories [20,21]: strong glass formers ($m < 30$), intermediate glass formers ($30 \leq m < 100$) and fragile glass formers ($m \geq 100$). The present result shows that the studied Pd–Si binary alloys possess fragility indexes closer to the lower limit of the intermediate glass formers. In addition, the fragility indexes of the other Pd-based metallic glasses [24,25] are also listed in Table 2 for a comparison. With increasing ΔT of these Pd-based glassy alloys, the fragility index roughly decreased except for Pd₈₀Si₂₀ and Pd₈₁Si₁₉ alloys. As known, it is generally acceptable that the larger ΔT , the more stable the glassy struc-

Table 2

The fragility m and the supercooled liquid range ΔT of the Pd–Si binary BMGs and some other metallic glasses (the heating rate dependent parameters are of 20 K/min).

Glassy alloys	ΔT	m
Pd ₈₀ Si ₂₀	63	56
Pd ₈₁ Si ₁₉	59	49
Pd ₈₂ Si ₁₈	57	47
Pd _{79.5} Au ₄ Si _{16.5} [24]	20	84
Pd _{77.5} Cu ₆ Si _{16.5} [25]	73	52
Pd ₄₀ Ni ₄₀ P ₂₀ [25]	88	41
Cu ₅₀ Zr ₅₀ [8]	47	62

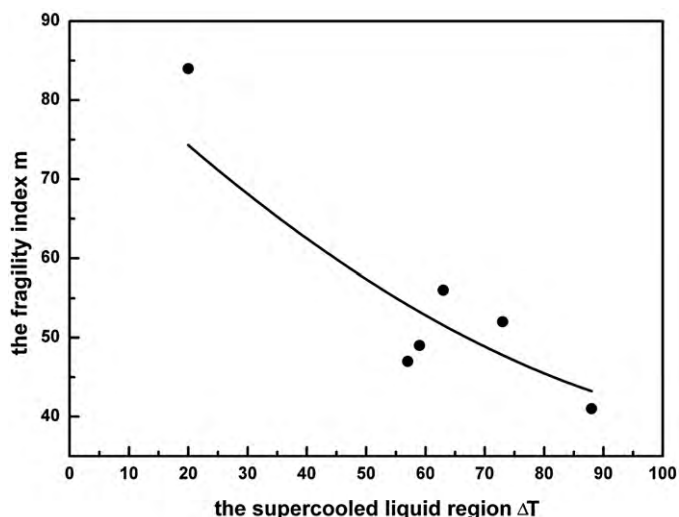


Fig. 4. The variation of the fragility m versus with the supercooled liquid range ΔT .

ture. Usually, wide ΔT indicates large glass forming ability [26]. Fig. 4 shows the changing trend of m with ΔT , the smaller m corresponds to larger ΔT and indicates larger glass forming ability. However, the changing trend for Pd–Si binary glassy alloys is reversed, showing that the best glass former is not the closest eutectic composition. It might be determined by its binary diagram without perfect symmetry [27]. 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 in Pd–Si alloys reported in Ref. [28]. It is needed to note that the fragility parameter of Pd–Si binary BMG is much smaller than that of Cu–Zr binary BMG (62) [8]. It indicates that the Pd–Si binary alloy might possess higher glass forming ability than Cu–Zr binary alloy.

4. Conclusions

It is found that Pd–Si binary bulk metallic glasses exhibit large activation energy for glass transition and crystallization, showing that the glassy structure and the supercooled liquid are very stable. In addition, the fragility index of Pd–Si glassy alloys was calculated to be 47–56, which is close to lower limit of the intermediate

glass formers, but larger than ternary Pd₄₀Ni₄₀P₂₀ glassy alloy. The smaller fragility index of Pd–Si glassy alloys does not correspond to the larger supercooled liquid region, which might be attributed to its asymmetric phase diagram or phase separation phenomenon.

Acknowledgements

This work was supported by The National Basic Research Program of China (2007 CB613905), The Natural Science Foundation of China (Grant Nos. 50671050 and 50971073), and the National Center for Nanoscience and Technology of China.

References

- [1] A.L. Drehman, A.L. Greer, D. Turnbull, *Appl. Phys. Lett.* 41 (1982) 716–718.
- [2] A. Inoue, K. Kita, T. Zhang, T. Masumoto, *Mater. Trans. JIM* 30 (1989) 722–725.
- [3] A. Inoue, T. Nakamura, T. Sugita, T. Zhang, T. Masumoto, *Mater. Trans. JIM* 34 (1992) 351–358.
- [4] A. Peker, W.L. Johnson, *Appl. Phys. Lett.* 63 (1993) 2342–2344.
- [5] Y. He, C.E. Price, S.J. Poon, *Phil. Mag. Lett.* 70 (1994) 371–377.
- [6] A. Inoue, *Acta Mater.* 48 (2000) 279–306.
- [7] D. Wang, Y. Li, B.B. Sun, M.L. Sui, K. Lu, E. Ma, *Appl. Phys. Lett.* 84 (2004) 4029–4031.
- [8] M.B. Tang, D.Q. Zhao, M.X. Pan, W.H. Wang, *Chin. Phys. Lett.* 21 (2004) 901–903.
- [9] D.H. Xu, B. Lohwongwatana, G. Duan, W.L. Johnson, C. Garland, *Acta Mater.* 52 (2004) 2621–2624.
- [10] K.F. Yao, F. Ruan, *Chin. Phys. Lett.* 22 (2005) 1481–1483.
- [11] L. Xia, D. Ding, S.T. Shan, Y.D. Dong, *J. Phys: Condense Matter* 18 (2006) 3543–3548.
- [12] L. Xia, W.H. Li, S.S. Fang, B.C. Wei, Y.D. Dong, *J. Appl. Phys.* 99 (2006) 026103.
- [13] K.F. Yao, F. Ruan, Y.Q. Yang, N. Chen, *Appl. Phys. Lett.* 88 (2006) 122106.
- [14] A. Inoue, W. Zhang, T. Tsurui, A.R. Yavari, A.L. Greer, *Phil. Mag. Lett.* 85 (2005) 221–229.
- [15] H.E. Kissinger, *US Bur Standards-J. Research*, 57 (1956) 217.
- [16] H.S. Chen, *Appl. Phys. Lett.* 29 (1976) 12–14.
- [17] Q. Qin, G.B. McKenna, *J. Non-cryst. Solids* 352 (2006) 2977.
- [18] Y.X. Zhuang, W.H. Wang, Y. Zhang, M.X. Pan, D.Q. Zhao, *Appl. Phys. Lett.* 75 (1999) 2392–2394.
- [19] W.H. Wang, L.L. Li, M.X. Pan, R.J. Wang, *Phys. Rev. B* 63 (2001) 052204.
- [20] C.A. Angell, *Science* 267 (1995) 1924.
- [21] R. Böhmer, K.L. Nagi, C.A. Angell, D.J. Plazek, *J. Chem. Phys.* 99 (1993) 4201.
- [22] C.A. Angell, *J. Non-cryst. Solids* 73 (1985) 1–17.
- [23] R. Brüning, K. Samwer, *Phys. Rev. B* 46 (1992) 11318.
- [24] H. Kato, T. Wada, M. Hasegawa, J. Saida, A. Inoue, H.S. Chen, *Scripta Mater.* 54 (2006) 2023.
- [25] H.S. Chen, *J. Non-cryst. Solids* 29 (1978) 223.
- [26] A. Inoue, *Mater. Trans. JIM* 36 (1995) 866.
- [27] D. Ma, H. Tan, D. Wang, Y. Li, E. Ma, *Appl. Phys. Lett.* 86 (2005) 191906.
- [28] S.Y. Hong, W.H. Guo, H.W. Kui, *J. Mater. Res.* 14 (1999) 3668.