Journal of Alloys and Compounds 434–435 (2007) 138–140

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

New Pd-based bulk glassy alloys with high glass-forming ability

Nobuyuki Nishiyama[a,*], Kana Takenaka[b], Takeshi Wada[b],
Hisamichi Kimura[c], Akihisa Inoue[a,c]

[a] *RIMCOF Tohoku University Laboratory, R&D Institute of Metals and Composites for Future Industries,*
Katahira 2-1-1, Sendai 980-8577, Japan
[b] *Graduate School, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan*
[c] *Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan*

Abstract

In order to realize biomedical applications of bulk glassy alloys, we have developed new Pd-based glassy alloys with Ni-free composition in the Pd–Pt–Cu–P system. As a result, it is revealed that the highest glass-forming ability is obtained at the composition of $Pd_{35}Pt_{15}Cu_{30}P_{20}$. Furthermore, the alloy can be formed into bulk glassy rods with diameters of up to at least 30 mm by fluxed water quenching. In this paper, we intend to clarify undercooling behavior and critical cooling rate for glass-formation in the new bulk glassy $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy.

Keywords: Bulk glassy alloys; Biomedical applications; Undercooling behavior; Critical cooling rate

1. Introduction

Bulk glassy alloys have attracted much attention because of their useful characteristics which are significantly different from those of crystalline alloys [1–4]. Focusing on Pd-based bulk glassy alloys, a cylindrical glassy rod with a diameter of 72 mm was prepared of a fluxed Pd–Cu–Ni–P [5]. Very recently, Pd- and Pt-based bulk glassy alloys have drawn increasing interest as biomedical materials. In this application field, it is necessary to develop a Pd-based bulk glassy alloy without Ni element. We have found that the partial replacement of Pd by Pt in $Pd_{40}Cu_{40}P_{20}$ alloy is effective for increasing maximum sample diameter and a Pd–Pt–Cu–P alloy with a particular composition can be formed into cylindrical glassy rod with a diameter of 30 mm [6]. These results suggest the Pd–Pt–Cu–P can be regarded as a new type of Pd-based bulk glassy alloy important for basic research and biomedical application. This paper presents undercooling behavior and critical cooling rate for glass-formation (R_c) of the new Pd–Pt–Cu–P bulk glassy alloy.

2. Experimental procedures

A master ingot with a composition of $Pd_{35}Pt_{15}Cu_{30}P_{20}$ was prepared by arc melting the mixtures of pure-Pd, -Ni, -Cu and pre-alloyed Pd–P in an argon atmosphere. In order to eliminate heterogeneous nuclei due to oxide contamination, a B_2O_3 flux treatment [7] was repeatedly carried out in a highly purified argon atmosphere (less than 10 ppm oxygen content) during alloy preparation. A high-vacuum high-temperature DSC (Mac Science HV/HT-DSC) was employed to construct a Continuous-Cooling-Transformation (CCT) diagram. Temperature deviation of the equipment from the cooling program was evaluated to be within ± 2.0 K. Each sample weighed 10 ± 0.5 mg to avoid internal temperature gradient in the sample during cooling measurement. The samples were initially heated to 1073 K and maintained at this temperature for 600 s to ensure complete melting. Then, the molten samples were cooled at different cooling rates (R) ranging from 0.667 to 0.017 K/s. For constructing a CCT diagram and determination of accurate critical cooling rate for glass-formation (R_c), the cross-sectional structure of the samples was examined with an optical microscope (OM) in polarized made as well as micro-area X-ray diffraction.

3. Results and discussion

Fig. 1 shows cooling DSC curves of the molten $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy obtained at R ranging from 0.667 to 0.017 K/s. A recalescence phenomenon due to precipitation of crystalline phases can be seen in each cooling DSC curve. Fig. 2a summarizes the on-set of recalescence temperature (T_x) as a function of cooling rate. A slight decrease in T_x with increasing R can be seen. Fig. 2b also summarizes the ratio of crystallization heat reduced by the heat of fusion ($\Delta H_x/\Delta H_f$) as a function of cooling rate. As seen in the figure, it is clear that the value of $\Delta H_x/\Delta H_f$ shows an asymptotic tendency to zero with increasing R. These results suggest that the R_c of the alloy will lie around 1 K/s and

---

[*] Corresponding author.
E-mail address: rimcofnn@imr.tohoku.ac.jp (N. Nishiyama).

0925-8388/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2006.08.249

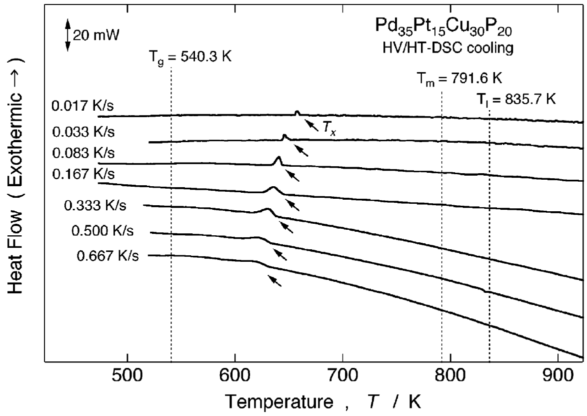

Fig. 1. Cooling DSC curves of molten $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy obtained at constant R ranging from 0.667 to 0.017 K/s.

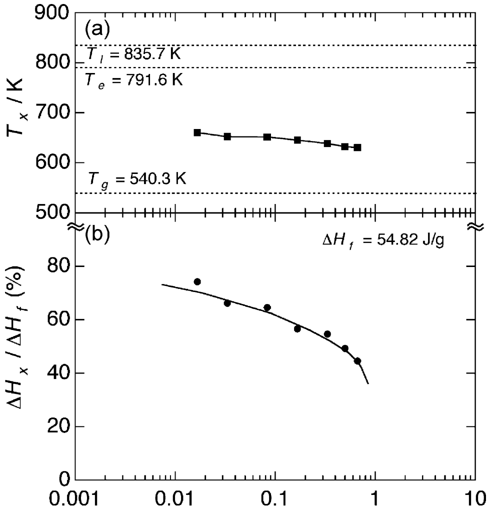

Fig. 2. (a) The on-set of recalescence temperature (T_x) as a function of cooling rate and (b) the ratio of crystallization heat reduced by heat of fusion ($\Delta H_x/\Delta H_f$) as a function of cooling rate.

fully glassy sample could not be obtained even at the highest R of 0.667 K/s.

Fig. 3 shows cross-sectional micrographs of the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ samples solidified at various R. The sample solidified at R of 0.017 K/s is composed of only a single crystalline grain.

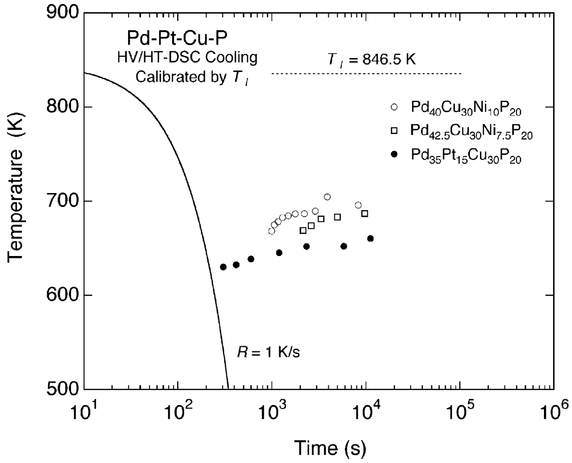

Fig. 4. CCT diagram for the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy constructed under various constant cooling rates.

In addition, it can be seen that the grain size drastically decreases and the number of crystalline grains increases with increasing R. XRD results (not shown here) reveal that each crystalline specimen is composed of $(Pd,Pt)_5P_2$, $(Pd,Pt)_{15}P_2$, $(Pd,Pt)_3P$ and CuPt eutectic structure and no metastable phase is found [6]. Here, it is worth noting that the structure of the sample solidified at the highest R of 0.667 K/s contains a glassy region in the vicinity of the center of the sample. This result is consistent with the R_c estimation of around 1 K/s.

The relation between T_x and R for the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy is plotted in a CCT diagram as shown in Fig. 4. Two kinds of Pd–Cu–Ni–P alloys are also shown for comparison. Based on the R_c estimation of 1 K/s for the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy, nose temperature (T_n) and incubation time (t_n) under constant cooling are estimated to be about 600 K and 200 s, respectively. One can notice that the undercooling for the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy is much deeper than those for the Pd–Cu–Ni–P alloys, while the liquidus temperature (T_l) of the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy (847 K) is almost the same as those for the Pd–Cu–Ni–P alloys (834 and 848 K). This result suggests that the nucleation frequency for the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy is much smaller than those for the Pd–Cu–Ni–P alloys. Taking account of the decreasing tendency in crystalline grain size shown in Fig. 3, it can be said that the

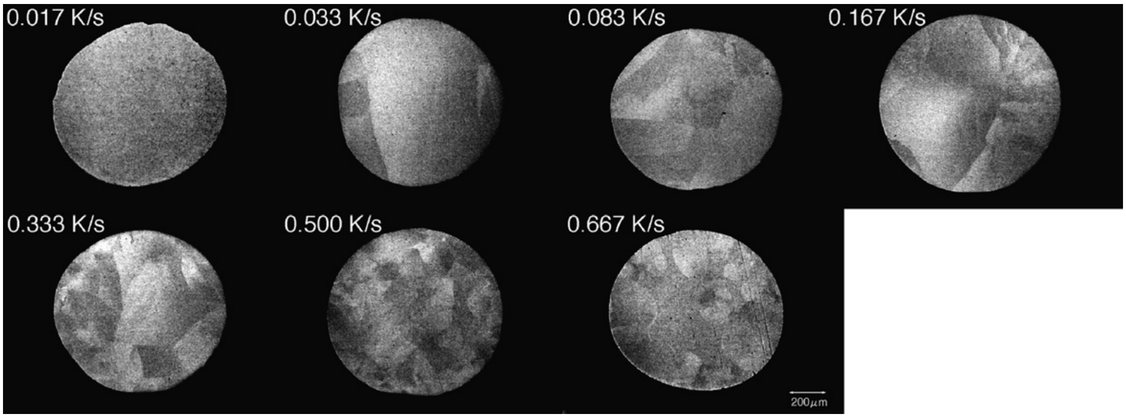

Fig. 3. Cross-sectional optical micrographs of the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ samples solidified at various R.

grain growth of the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy will be much faster than that of Pd–Cu–Ni–P alloy.

4. Conclusions

Undercooling behavior and critical cooling rate for glass-formation for the $Pd_{35}Pt_{15}Cu_{30}P_{20}$ alloy were investigated. As a result, the critical cooling rate for glass-formation of the alloy is estimated to be about 1 K/s. It is also found that the grain growth rate of the alloy is much higher than that of Pd–Cu–Ni–P alloy. However, the highly processable feature due to the high glass-forming ability of the alloy is applicable for biomedical applications.

References

[1] A. Inoue, Mater. Trans. JIM 36 (1995) 866–875.

[2] A. Inoue, Acta Mater. 48 (2000) 279–306.

[3] A. Inoue, Mater. Sci. Eng. A 304–306 (2001) 1–10.

[4] A. Inoue, A.R. Yavari, W.L. Johnson, R.H. Dauskardt (Eds.), Supercooled Liquid Bulk Glassy and Nanocrystalline State of Alloys, MRS, Warrendale, 2001, pp. L12.13.1–L12.13.6.

[5] A. Inoue, N. Nishiyama, T. Matsuda, Mater. Trans. JIM 37 (1996) 181–184.

[6] K. Takenaka, T. Wada, N. Nishiyama, H.M. Kimura, A. Inoue, Mater. Trans., in press.

[7] H.W. Kui, A.L. Greer, D. Turnbull, Appl. Phys. Lett. 45 (1984) 615.