Undercooling Behavior and Critical Cooling Rate of Pd–Pt–Cu–P Alloy

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In order to realize biomedical applications of bulk glassy alloys, we have developed new Pd-based glassy alloys with Ni-free composition in Pd–Pt–Cu–P system and it is revealed that the highest glass-forming ability is obtained at a composition of Pd₃₅Pt₁₅Cu₃₀P₂₀. In addition, the alloy can be formed into bulk glassy rods with diameters of up to at least 30 mm by fluxed water quenching. In order to clarify the critical cooling rate for glass-formation, undercooling behavior and crystal growth rate are also discussed. Crystallization of the alloy under continuous cooling is mainly dominated by surface nucleation. Apparent crystal growth rate of the alloy at 0.73 T_m is evaluated to be 5.2×10^{-6} m·s⁻¹ and this value is four orders of magnitude higher than that of previous Pd₄₀Cu₃₀Ni₁₀P₂₀ at the same degree of undercooling.

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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)} In particular, bulk glassy alloys are appropriate for biomedical applications due to their high strength, low Young's modulus, excellent corrosion resistance and viscous flow properties. Recently, Pd- and Pt-based bulk glassy alloys have drawn increasing interest as biomedical materials. Focusing on Pd-based bulk glassy alloys, a Pd–Cu–Ni–P alloy can be formed into cylindrical glassy rod with a diameter of 72 mm⁵⁾ and the maximum size of the alloy may be enough to use biomedical or dental materials. However, the alloy contains an unsuitable element, that is Ni, which will cause human allergy. In their application field, it is necessary to develop a Pd-based bulk glassy alloy without Ni element. Very recently, we have found that the partial replacement of Pd by Pt in Pd₄₀Cu₄₀P₂₀ alloy is effective for the increases in maximum sample diameter and Pd–Pt–Cu–P alloy with a particular composition can be formed into a cylindrical rod with a diameter of 30 mm.⁶⁾ The newly developed alloy also shows high strength of 1410 MPa, high fracture strain of 0.017 and low Young's modulus of 83.0 GPa under tensile load. These results suggest that the newly developed Pd–Pt–Cu–P bulk glassy alloy can be regarded as a new type of Pd-based bulk glassy alloy, which is 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. Furthermore, nucleation behavior and crystal growth rate will be also discussed.

2. Experimental Procedures

A master ingot with a composition of Pd₃₅Pt₁₅Cu₃₀P₂₀ was prepared by arc melting the mixtures of pure-Pd, -Ni, -Cu and pre-alloyed Pd–P and Pt–P in an argon atmosphere. In order to eliminate heterogeneous nuclei due to oxide contamination, a B₂O₃ flux treatment⁷⁾ 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 in order 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 spherical sample weighed 10 ± 0.5 mg to avoid the internal temperature gradient of sample during cooling measurement. The samples were initially heated to 1073 K at a heating rate of 0.67 K/s 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, cooling DSC curves are analyzed in order to evaluate onset of crystallization temperature (T_x) and incubation time for crystallization (t_x). In order to determine accurate critical cooling rate for glass-formation (R_c), the cross-sectional structure of the samples was examined with an optical microscope (OM) using a polarized observation and micro-area X-ray diffraction.

3. Results

Figure 1 shows cooling DSC curves of the molten Pd₃₅Pt₁₅Cu₃₀P₂₀ alloy obtained at different R . A recalescence phenomenon due to crystallization can be clearly seen in each cooling DSC curve. Figure 2(a) summarizes the T_x as a function of R . A slight decrease in T_x with increasing R can be seen. Figure 2(b) also summarizes the ratio of crystallization heat reduced by 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 as according to the increasing R . These results suggest that the R_c of the alloy will be laid around 1 K/s, while the fully glassy sample could not be obtained even at the highest R of 0.667 K/s.

Figure 3 shows the cross-sectional micrographs of the Pd₃₅Pt₁₅Cu₃₀P₂₀ samples solidified at various R . The sample solidified at R of 0.017 K/s is composed of only a single crystalline grain. In addition, it can be seen that the grain size drastically decreases and the number of crystalline grains

Fig. 1 Cooling DSC curves of the molten $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ 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 R and (b) the ratio of crystallization heat reduced by the heat of fusion ($\Delta H_x / \Delta H_f$) as a function of R .

increases with increasing R . Figure 4 shows the XRD patterns taken from the obtained samples, revealing that each crystalline grain is composed of $(\text{Pd,Pt})_5\text{P}_2$, $(\text{Pd,Pt})_{15}\text{P}_2$, $(\text{Pd,Pt})_3\text{P}$ and CuPt eutectic structure and no meta-stable phase is found.⁶⁾ Here, it is worth to note 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 $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ alloy is plotted in a CCT diagram as shown in Fig. 5. The crystallization temperatures T_x for 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 $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ alloy, nose temperature (T_n) and incubation time (t_n) under constant cooling are assumed to be about 600 K and 200 s, respectively. One can notice that the undercooling for the

Fig. 4 XRD patterns of the $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ samples solidified at various constant R .

Fig. 3 Cross-sectional micrographs of the $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ samples solidified at various constant R .

Fig. 5 CCT diagram for the $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ alloy constructed under various constant R .

Fig. 6 Enlarged cross-sectional micrograph of the $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ sample solidified at 0.667 K/s.

$\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ alloy is much deeper than those for the Pd–Cu–Ni–P alloys, while the liquidus temperature (T_l) of the $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ 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 $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ alloy is much smaller than those for the Pd–Cu–Ni–P alloys. On the other hand, the grain size of crystals shown in the Fig. 3 is much larger than that for the Pd–Cu–Ni–P alloys reported previously⁸⁾ even at the same R . Therefore, it can be said that the grain growth of the $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ alloy will be much faster than that of Pd–Cu–Ni–P alloy. However, it is concluded that the low R_c of about 1 K/s and the formation of a bulk glassy rod with a diameter of 30 mm in Ref. 6) are quite useful for biomedical applications.

4. Discussion

Here, we discuss about the nucleation behavior and crystal growth rate of the alloy. Figure 6 shows enlarged cross-sectional micrographs of the $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ samples

Fig. 7 Micro XRD patterns taken from regions corresponding A and B in the Fig. 8.

Fig. 8 A relationship between apparent crystal growth rate (u_c) and reduced temperature for the undercooled $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ alloy. The previous result for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ alloy is also plotted for comparison.

solidified at 0.667 K/s. The structure of the sample can be clearly divided into two parts represented featureless A and B with some contrast regions. Corresponding micro XRD patterns are given in Fig. 7. As seen in the figure, the micro

XRD pattern taken from the A-region is consist of only halo pattern, revealing that the central region of the sample is composed of glassy phase. On the other hand, the pattern from the B-region can be identified as $(\text{Pd,Pt})_5\text{P}_2$, $(\text{Pd,Pt})_{15}\text{P}_2$, $(\text{Pd,Pt})_3\text{P}$ and CuPt phases. Taking the micro XRD pattern taken from only single crystal grain into account, each crystal grains are precipitated an eutectic manner. In addition, the crystallization of the sample is mainly dominated by surface nucleation. The longest crystal growth distance is evaluated to be $280\text{ }\mu\text{m}$ (represented with arrow). As seen the cooling DSC curve at a rate of $0.667\text{ K/sin Fig. 1}$, the time during crystallization completing and reduced crystallization temperature are estimated to be 54 s and $0.73\text{ }T_{\text{m}}$, respectively. These values are plotted as a relationship between apparent crystal growth rate (u_{c}) and reduced temperature in Fig. 8. Previous result for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ alloy is also plotted for comparison. At the same reduced temperature (at $0.73\text{ }T_{\text{m}}$), u_{c} for the undercooled $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ alloy ($9.8 \times 10^{-10}\text{ m}\cdot\text{s}^{-1}\text{c}$). This four orders of magnitude difference in crystal growth rate causes twelve orders of magnitude difference in volume fraction of crystals. It is therefore concluded that the difference in R_{c} for the Pd-Pt-Cu-P and Pd-Cu-Ni-P alloys is attributed to the difference in crystal growth rate.

5. Conclusions

Undercooling behavior and critical cooling rate for glass-formation for the $\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$ 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.

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