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Crystallization accelerated by ultrasound in Pd-based metallic glasses

Tetsu Ichitsubo [a,*], Eiichiro Matsubara [a], Kazuhiro Anazawa [b], Nobuyuki Nishiyama [c]

[a] *Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*
[b] *Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[c] *RIMCOF, R&D Institute of Metals and Composites for Future Industries, Sendai 980-8577, Japan*

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Abstract

We have investigated the crystallization behavior of $Pd_{40}Ni_{40}P_{20}$ and $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ bulk metallic glasses under ultrasonic (US) vibrations of MHz frequencies. Both metallic glasses were isothermally annealed at various temperatures under US vibrations, and the duration till the crystallization is completed (crystallization time) under US vibrations is compared with that without US vibrations. In both cases, the crystallization time for the US annealing was found to be much shorter than that without US vibrations. The X-ray diffraction profiles reveal that the crystalline phases obtained after the US annealing are identical to those obtained by the ordinary annealing without vibrations.

Keywords: Metallic glasses; Rapid solidification; Quenching; Phase transitions; X-ray diffraction; Ultrasonics

In the last decade, bulk metallic glasses (BMG) having an excellent glass-forming ability (GFA) have been discovered in multicomponent systems [1]. Pd-based metallic glasses, such as $Pd_{40}Ni_{40}P_{20}$ or $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, are considerably stable metallic glasses available at present. Recently, we have found that low-temperature crystallization occurs around T_g under ultrasonic vibrations, accompanied by a large increase in the internal friction [2–4]. Similar anomalous behavior was also observed by other researchers. For example, Mizubayashi et al. [5,6] showed that pulsed electric currents accelerate crystallization of some kinds of amorphous alloys at a temperature far below the normal crystallization temperature. In addition, reduction of the glass transition and crystallization temperatures (T_g and T_x) is also recognized in the ultrasonic pulse-echo measurements for a $Zr_{55}Al_{10}Ni_5Cu_{30}$ metallic glass by Keryvin [7]. In this study, we perform isothermal annealing under ultrasonic vibrations for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Pd_{40}Ni_{40}P_{20}$, and compare the difference in the crystallization behavior under ultrasound between these alloys. The main purpose of this work is to investigate the presence or absence of difference between the US-induced crystalline phases and normally formed phases.

Alloy ingots of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Pd_{40}Ni_{40}P_{20}$ (at.%) bulk metallic glasses were used in this work. The characteristic temperatures, T_g and T_x (crystallization temperature), were determined by the differential scanning calorimeter (DSC) with different heating rates. They were approximated to be $T_g \sim 295\,^{\circ}C$ and $T_x \sim 370\,^{\circ}C$ in both glassy alloys for a heating rate of $5\,^{\circ}C$/min. In order to carry out annealing at elevated temperatures under US vibrations (US annealing), we employed the electromagnetic acoustic resonance (EMAR) method. The details of the EMAR technique were described in literature [2,3]. The samples of cylindrical shape (about Ø3 mm × 4 mm) were used for the US annealing. The resonance frequencies f_r of the cylindrical samples were monitored in a sub/low-MHz frequency range. We can detect the sample crystallization by the marked change in the resonance frequencies (i.e., elastic constants). Since the EMAR method utilizes the eddy current on the sample surface, which is induced by the coil currents, its heating effect must be taken into account. To measure the sample temperature accurately, we checked the sample temperature and furnace temperature by using two Pt–PtRh thermocouples. In actual experiments, a dummy sample was also prepared in the electromagnetic acoustic transducer (EMAT) coil for measuring the sample-surface temperature T_s; T_s is used for the figures shown in this paper. The crystalline phases formed in the samples were examined by X-ray diffraction using Cu Kα radiation.

Fig. 1 shows the time–temperature–transformation (TTT) diagram for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Pd_{40}Ni_{40}P_{20}$ with or without ultrasonic vibrations, where the temperature is normalized by the melting (liquidus) temperature. Without US vibrations, the reduced crystallization temperature T/T_m of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ is higher than that of $Pd_{40}Ni_{40}P_{20}$, which means that the

* Corresponding author.
E-mail address: tichi@mtl.kyoto-u.ac.jp (T. Ichitsubo).

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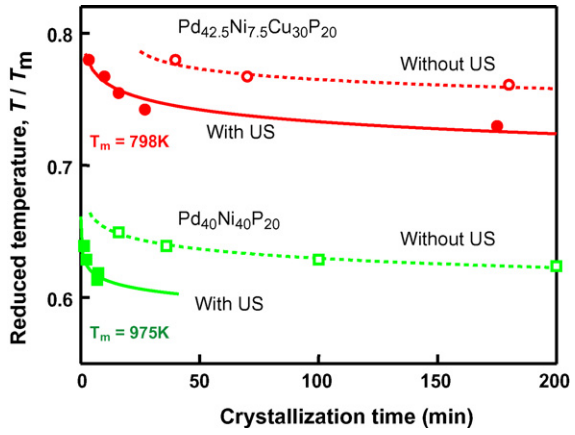

Fig. 1. Time–temperature–transformation diagram for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Pd_{40}Ni_{40}P_{20}$ with or without ultrasonic vibrations. The sample-surface temperature T_s is used for the TTT diagram, and the temperature is normalized by the melting (liquidus) temperature.

crystallization is hard to occur for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ than for $Pd_{40}Ni_{40}P_{20}$, that is, the former alloy is thermally more stable than the latter. In the case of US annealing, we can see that the crystallization is very accelerated by the US annealing at about 1 MHz frequency for both alloys. Although the crystallization behaviors under US vibrations are similar to each other, it is found from the notable change around zero time that the US-accelerated crystallization for $Pd_{40}Ni_{40}P_{20}$ is easier to occur than that for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, which may reflect the thermal stability.

Fig. 2 shows the X-ray diffraction profiles of the two glassy alloys (upper: $Pd_{40}Ni_{40}P_{20}$, lower: $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$). The US-annealing treatments were performed below T_x (at 5 °C/min in DSC), and to confirm the equilibrium crystalline phases, the samples were annealed at the relatively high temperature annealing (450 °C > T_x) for long duration. For $Pd_{40}Ni_{40}P_{20}$, the profiles obtained after the US annealing are quite similar to that for the normal annealing without US vibrations at high temperature (450 °C). Namely, the induced crystalline phases are almost identical to the equilibrium crystalline phases. In contrast, for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, the profiles of the US-annealed sample (330 °C for 17 min) is considerably different from that obtained for the normal annealing at high temperatures (450 °C for 360 min), which indicates that the induced crystalline phases are not the same as the equilibrium crystalline phases. However, the difference can be attributed to the difference in the annealing temperatures for the two profiles. Then, we performed the low-temperature annealing for long duration, 330 °C for 25 h. It is found that the X-ray profile also differs from the profiles of equilibrium crystalline phases obtained after the high-temperature (450 °C) annealing but resembles that obtained for the US annealing at low temperature. (Namely, in the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ system, the metastable phases are formed at relatively low temperatures, regardless of the presence of the US vibrations.) Consequently, the US annealing merely enhances the crystallization rate (at low temperature) but does not induce new different phases.

In conclusion, we have investigated the effects of the ultrasound vibrations on the crystallization behavior of $Pd_{40}Ni_{40}P_{20}$ and $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$. It is concluded that the US vibrations accelerates the crystallization in both glassy alloys even at low temperatures near the glass transition temperature but do not produce the particular (anomalous) phases.

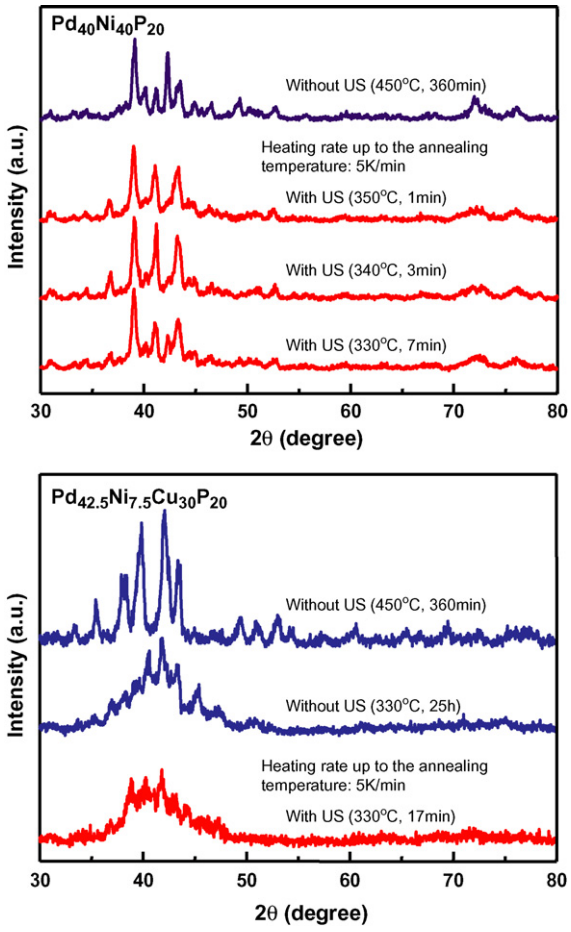

Fig. 2. X-ray diffraction profiles obtained for the samples subjected to various heat treatments with or without ultrasonic vibration (upper: $Pd_{40}Ni_{40}P_{20}$, lower: $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$).

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