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Influences of hydrostatic pressure during casting and Pd content on as-cast phase in Zr-Al-Ni-Cu-Pd bulk alloys

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The influences of sample diameter (D), Pd content (x), and hydrostatic pressure (P) in a chamber during casting on the structure of as-cast Zr₆₅Al₇.₅Ni₁₀Cu₁₇.₅₋ₓPdₓ (x=10, 17.5 at. %) bulk alloys were investigated. Zr₆₅Al₇.₅Ni₁₀Cu₇.₅Pd₁₀ and Zr₆₅Al₇.₅Ni₁₀Pd₁₇.₅ alloys (D=3 mm) cast in a vacuum chamber (P~4.0×10⁻³ Pa) were mainly of the tetragonal-Zr₂Ni equilibrium phase and nanosize icosahedral primary phase, respectively, while the same alloys cast in inert argon gas at atmospheric pressure (P~0.1 MPa) were of the single glassy phase. Due to the higher cooling rate obtained by decreasing the sample diameter (D=2 mm) even in the vacuum chamber, the Zr₆₅Al₇.₅Ni₁₀Pd₁₇.₅ alloy was still of the icosahedral phase, while the Zr₆₅Al₇.₅Ni₁₀Cu₇.₅Pd₁₀ alloy froze into a single glassy phase. These results indicate that the temperature- and time-transformation curves for the icosahedral and subsequent equilibrium phase formations in the alloy system shifts to a shorter time side with decreasing P, and the pressure sensitivity of the icosahedral phase formation increases with x. © 2004 American Institute of Physics. [DOI: 10.1063/1.1790028]
and 2(b) show bright-field TEM images of 17.5Pd3A with a selected-area electron diffraction pattern and those of 17.5Pd3V with a nanobeam diffraction pattern, respectively. One can confirm that 17.5Pd3A exhibits a glassy phase, but 17.5Pd3V consists mainly of QC precipitates with an average diameter less than 50 nm. The rod diameters of 17.5Pd3A, 17.5Pd3V, 10Pd2V, and 10Pd3V are 3 mm. Therefore, the cooling rates are considered to be approximately the same for these cast alloys because the heat transfer of the mould cast method is achieved through the copper walls and the contribution of the atmospheric inert gas can be neglected. However, for the two compositions, x = 10 and 17.5, the samples cast at P = 0.1 MPa are of the single glassy phase, while those cast at P = 4 × 10^{-3} Pa contains the crystalline phases. Therefore, one can conclude that this difference in as-cast structure is due to the difference in hydrostatic pressure in the chamber. The decrease in P during the casting process decreases GFA, i.e., it enhances the devitrification in this alloy system.

Figure 3(a) shows the DSC curves for 10Pd3A, 10Pd2V, and 10Pd4V, and Fig. (b) those for 17.5Pd3A, 17.5Pd3V, and 17.5Pd2A. According to the reports on Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5−x}Pd_{x} (x = 5 – 17.5) by Saida et al.,

11 the first exothermic peak is due to the nanocrystallization in SCL and the second one is due to the subsequent transformation from the QC phase to the equilibrium phase, e.g., tetragonal-Zr_{2}Ni, Zr_{2}Cu, etc. The first exothermic peak in the DSC curve for 17.5Pd3V whose XRD pattern [Fig. 1(b)] shows the existence of the QC phase completely disappears, but the second one remained. On the other hand, not only the first peak but also the second peak almost disappears in 10Pd3V. Therefore, we have observed the tetragonal-Zr_{2}Ni equilibrium phase in 10Pd3V [Fig. 1(a)].

Hydrostatic pressure may influence the thermodynamic potential energy barrier of nucleation in the SCL region during cooling. The nucleation rate I is expressed by

\[ I = \frac{I_{0}}{\exp \left( \frac{\Delta G^* + Q_{n}}{k_{B}T} \right)} \]

where \( I_{0}, k_{B}, Q_{n}, \) and \( \Delta G^* \) are a constant, Boltzmann’s constant, the activation energy for the transport of an atom across the interface of an embryo and the free energy required to form a nucleus of critical size, respectively. The dependence of external pressure on the devitrification of SCL during heating is discussed in some reports. According to Jiang et al.,

12 the nucleation work, \( \Delta G^* + Q_{n} \), can be influenced by external pressure. \( \Delta G^* \) is proportional to \( \sigma^{3}/(p\Delta V + \Delta G)^{2} \), where \( \sigma \), \( \Delta V \), and \( \Delta G \) are the interfacial energy of the crystal, molar volume, and free-energy changes from SCL to the crystalline phase, respectively, \( \sigma \) and \( \Delta G \) are considered to be independent of external pressure. In general, the increase in hydrostatic pressure reduces atomic mobility, and therefore, \( Q_{n} \) increases. The pressure effect on \( \Delta G^* + Q_{n} \) in SCL could be determined by \( \Delta G^* \) and \( Q_{n} \), therefore the sign of \( \Delta V \). In the case of the Zr-Al-Ni-Cu-Pd system, its GFA increases with increasing \( P \) [Fig. 1(b)]. This result allows the sign of \( \Delta V \) to be both positive and negative. However, Holzer and Kelton

13 and Jiang et al.

12 reported an increase in molar volume by the quasicrystallization of the Al_{2}Cu_{15}V_{10} and Zr_{7}Pd_{30} alloys, respectively. We can fairly assume that the sign of \( \Delta V = \Delta V_{Q} - \Delta V_{SCL} \) for the Zr-Al-Ni-Cu-Pd metallic glass is positive. Therefore, both \( \Delta G^* \) and \( Q_{n} \) increase with increasing external pressure. However, PAV may be much smaller than \( \Delta G \); therefore \( \Delta G^* \) varies little at \( P = 0.1 \) MPa and \( 4 \times 10^{-3} \) Pa. The reason why

\[ \Delta V (=\Delta V_{Q} - \Delta V_{SCL}) \]
the chamber pressure strongly influences the nucleation behavior in the alloys is not cleared in this letter.

Incubation time for the nucleation could be the inverse of the nucleation rate, $I^{-1}$; thus it increases with decreasing temperature. Meanwhile, the viscosity of SCL increases according to the Vogel-Fulcher-Tammann formula\textsuperscript{14} and the corresponding relaxation time, $\tau$, increases with decreasing temperature. Therefore, during the cooling, the precipitation of the primary phase and the vitrification of alloy melt are competing phenomena. If $I^{-1}$ maintained larger than $\tau$, SCL finally freezes into a single-glassy phase at $T^*_f$; otherwise, the precipitation occurs during the cooling. To investigate the influence of cooling rate on the structure of as-cast $\text{Zr}_{65}\text{Al}_{17.5}\text{Ni}_{10}\text{Cu}_{7.5-x}\text{Pd}_x$ alloys, the XRD and DSC results of the samples of $D=2$ mm are shown in Figs. 1 and 3, respectively. 17.5Pd2V was mainly of the QC phase, the same as 17.5Pd3V, i.e., $I^{-1} < \tau$, on the other hand, 10Pd2V froze into a single glass, i.e., $I^{-1} > \tau$.

Based on the above results, schematic illustrations of the cooling route in the TTT curves are summarized in Figs. 4(a) and 4(b) for the 10Pd and 17.5Pd series, respectively. Because the reduced glass-transition temperatures, $T_f/T_1$, of these two alloys are almost the same at $\sim 0.55$, the TTT curves of the primary QC phase for these alloys at $P \approx 0.1 \text{ MPa}$ can be drawn at almost the same time positions [see solid lines in Figs. 4(a) and 4(b)], respectively. In addition, the time interval between the primary QC phase formation and the subsequent equilibrium (equi.) phases should be larger for 17.5Pd and smaller for 10Pd [see solid lines in Figs. 4(a) and 4(b)] because the thermal stability of the QC phase increases with Pd content.\textsuperscript{2,11} The TTT curves of the QC and equi. shift to the shorter time side with decreasing $P$ and are drawn by dotted lines. Considering the results in Figs. 1 and 3, the nose points of the QC and Equi. curves at $P = 4 \times 10^{-3}$ Pa should be placed between the cooling lines of $D=2$ and 3 mm for the 10Pd alloy in Fig. 4(a). On the other hand, these cooling lines should be placed between the nose points of the QC and equi. curves for the 17.5 Pd alloy in Fig. 4(b). These results indicate that the influence of pressure on TTT curves increases with increasing Pd content.

In summary, the influences of sample diameter, Pd content, and hydrostatic pressure in a chamber during the casting on the structure of as-cast $\text{Zr}_{65}\text{Al}_{17.5}\text{Ni}_{10}\text{Cu}_{17.5-x}\text{Pd}_x$ ($x = 10, 17.5 \text{ at.} \%$) bulk alloys were investigated. It is concluded that the nose position of TTT-curves for icosahedral and subsequent equilibrium phases shift to a shorter time side with decreasing hydrostatic pressure in the chamber during casting. The pressure sensitivity of icosahedral phase formation increases with Pd content. Lastly, the control of hydrostatic pressure during casting may open up fabrication processes for bulk metallic glasses and bulk nanostructured alloys.

\textsuperscript{11}J. Saida, M. Matsuhihta, and A. Inoue, Mater. Trans., JIM \textbf{41}, 1505 (2000).