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# Origin of the Effect of the Gas Atmosphere during Mold-Casting $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ Bulk Glassy or Nano-Quasicrystal-Forming Alloy

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We provide a quantitative analysis of the importance of the gas species and pressure during mold-casting process on the apparent glass-forming ability (GFA) of  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy, recently reported by Kato *et al.* (*e.g.* Scripta Mater. 51 (2004) 13). The cooling characteristics are found to depend in remarkable detail on the gas species and the pressure existing in the cavity between the melt and the mold presumably formed during the cooling process. This understanding has been successfully applied to significantly improve the critical diameter of the glassy rods to 7 mm in an atmosphere of helium environment from 5 mm in that of argon. [doi:10.2320/matertrans.MF200619]

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## 1. Introduction

In recent years, a number of bulk metallic glasses with extremely high glass-forming ability (GFA) have been reported in Zr-based multicomponent alloy systems.<sup>1,2)</sup> The high thermal stability of supercooled liquid (SCL) or glassy state in these systems has attracted much scientific interest.<sup>3)</sup> The thermal stability of SCL is thought to correlate to the significant structural/compositional differences between local short-range order and crystalline phase, and the close-packed structure in which long-range atomic diffusion required for crystallization is hindered. The latter aspect might stimulate an expectation that hydrostatic pressure affects the diffusivity and, thus, the devitrification of SCL. In fact, there have been many studies reporting the effect of external pressure, which was applied mostly in GPa-order, on crystallization, glass transition or structural relaxation of metallic glasses.<sup>4–11)</sup> Kato *et al.* have recently reported the influence of hydrostatic chamber-pressure during casting on as-cast structure in Zr-Al-Ni-Cu-Pd alloys.<sup>12,13)</sup> It demonstrated that the as-cast structure of the alloys was different between the samples prepared under a vacuum condition and under an atmospheric pressure of argon. The work suggested that with decreasing pressure the temperature-time-transformation (T-T-T) curves for the primary icosahedral-quasicrystalline (QC) and subsequent equilibrium phase formations in the alloy systems may shift toward a shorter time scale. The origin of such a phenomenon was thought to arise from the correlation between the pressure and the homogenous nucleation rate. However, the report noted that the reason was still unclear, because the order of the pressure, by calculation, was too low to give a significant effect on the nucleation behavior.

In this work, we report an investigation on the origin of the different as-cast structures of the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy during mold-casting under various atmospheres by analyzing the cooling characteristics of the samples. The results indicate that the cooling characteristic of alloy, rather than

the hydrostatic pressure effect on nucleation behavior as what discussed in Kato's work,<sup>12,13)</sup> is responsible for the different as-cast structures. The cooling characteristic is found to be affected by gas used as the atmosphere during mold-casting. A cavity between the mold-wall and the sample is considered to form during cooling process. The species and pressure of gas atmosphere existing in the cavity affect the heat-transfer effectiveness, which in turn influence the cooling behavior of the samples. The formation of permanent cavity occurs when temperature of the cast sample arrives at a low-temperature side of the SCL region (*i.e.*  $T < T_g + 160$  K, where  $T_g$  is the glass transition temperature), which is coincident with the fairly considered location of T-T-T curve for the primary crystallization of icosahedral QC phase in the present alloy. This situation leads to the variation in as-cast structure of the present alloy with the change of casting atmosphere.

## 2. Experimental Procedure

An ingot of  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy was prepared by arc-melting mixtures of pure elements in an argon atmosphere. The ingot was crushed into pieces and filled into a quartz tube and then inductively melted up to 1273 K (*i.e.*, about 100 K above the liquidus temperature ( $T_l$ ) of alloy) under one of the following controlled atmospheres: vacuum of  $2 \times 10^{-3}$  Pa, Ar of 1 kPa, Ar of  $10^5$  Pa (atmospheric pressure), or He of  $10^5$  Pa. A pyrometer was used to monitor temperature of the melts. The melts were then cast into a copper mold to produce rods with 3–8 mm in diameter and 50 mm in length. The rod samples of 3 mm in diameter prepared under such casting atmospheres were designated as Z-17.5Pd3-V (vacuum), Z-17.5Pd3-1k (Ar of 1 kPa), Z-17.5Pd3-A (Ar of  $10^5$  Pa) and Z-17.5Pd3-H (He of  $10^5$  Pa). Temperature change of the melts during cooling was recorded by a thin (0.3 mm in diameter) K-type thermocouple which was connected to an analog-to-digital signal converter (Graphtec GL500) to obtain the cooling (time-temperature) curves. The thermocouple was placed at the bottom of the mold. The data interval was 1 ms. The structure of the samples was examined by X-ray diffractometry with monochromatic Cu-K $\alpha$  radiation.

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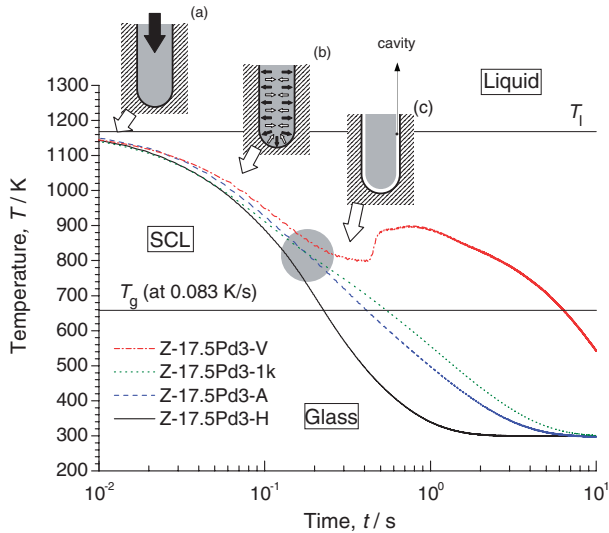


Fig. 1 Cooling (time-temperature) curves of the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy cast under various casting atmospheres, *i.e.* vacuum of  $2 \times 10^{-3}$  Pa (Z-17.5Pd3-V), Ar of 1 kPa (Z-17.5Pd3-1k), Ar of  $10^5$  Pa (Z-17.5Pd3-A), and He of  $10^5$  Pa (Z-17.5Pd3-H). A schematic description corresponding to the cooling process is also shown: (a) melts just after fill the mold, (b) competition between the volume-shrinkage and the flow, (c) formation of a stable cavity between the sample and the mold-wall. The dashed circle points roughly the position of the deflection in the cooling curve.

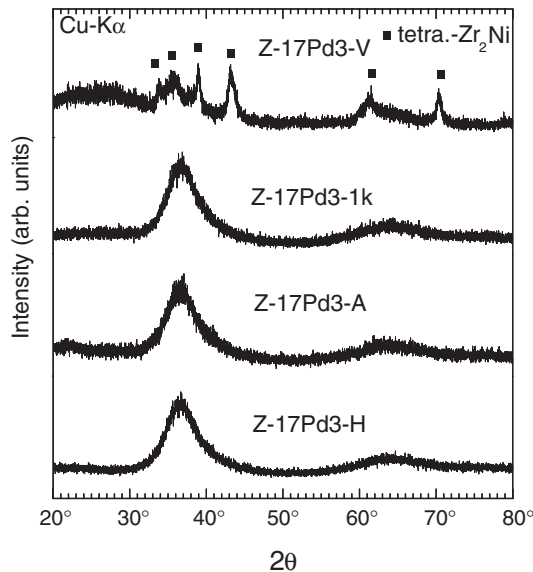


Fig. 2 X-ray diffraction patterns of the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy of 3 mm  $\phi$  cast under various casting atmospheres, *i.e.* Z-17.5Pd3-V (vacuum of  $2 \times 10^{-3}$  Pa), Z-17.5Pd3-1k (Ar of 1 kPa), Z-17.5Pd3-A (Ar of  $10^5$  Pa) and Z-17.5Pd3-H (He of  $10^5$  Pa).

### 3. Results and Discussion

#### 3.1 Cooling curve and as-cast structure

Cooling curves obtained from measurement of sample temperature during cooling are seen in Fig. 1. Corresponding X-ray diffraction (XRD) patterns of the as-cast samples are shown in Fig. 2. Firstly, let us discuss for the cases of Z-17.5Pd3-A and Z-17.5Pd3-V, since these samples were also studied in Kato's work.<sup>12,13</sup> The cooling curves apparently

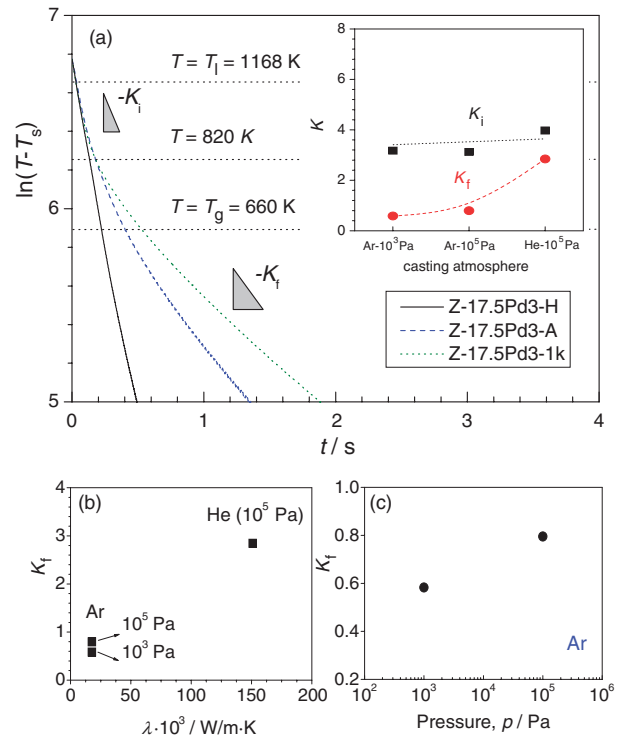


Fig. 3 (a) Plot of  $\ln(T - T_s)$  versus  $t$  for the cooling curve of Z-17.5Pd3-1k (Ar of 1 kPa), Z-17.5Pd3-A (Ar of  $10^5$  Pa) and Z-17.5Pd3-H (He of  $10^5$  Pa) and experimental cooling-constant at the initial stage of cooling process,  $K_i$ , and at the subsequent cooling process,  $K_f$ , versus casting atmosphere (inset). Plot of  $K_f$  in correlation with: (b) gas thermal conductivity  $\lambda$  or, (c) pressure of Ar gas applied as the casting atmosphere.

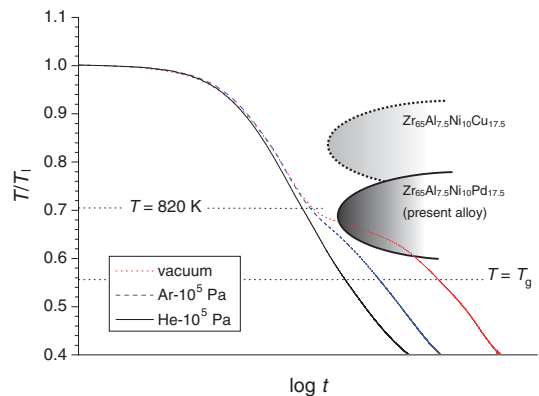


Fig. 4 A schematic illustration describing the position of crystallization curves in a T-T diagram of  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  and  $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$  alloys relative to the cooling curves of a sample cast under various casting atmospheres.

show that temperature decreases generally at a little higher rate in Z-17.5Pd3-A than in Z-17.5Pd3-V. Suffering from a relatively low cooling rate, the Z-17.5Pd3-V exhibits a recalescence corresponding to crystallization which cannot be bypassed during cooling under vacuum condition. The crystallization in Z-17.5Pd3-V corresponds to the formation of an equilibrium tetragonal- $Zr_2Ni$  phase as confirmed by the XRD pattern of the as-cast sample (see Fig. 2). On the other hand, the cooling curve of Z-17.5Pd3-A does not show any recalescences as the curve goes down smoothly from high

temperature to the room one with increase of elapsing time. Meanwhile, the XRD scan to the as-cast sample resulted in a typically broad pattern corresponding to a glassy structure.

If we take a look carefully to each cooling curve, there is a deflection reflecting deviation of cooling characteristic between the initial and subsequent stages; the deflection is observed at  $T \sim 820$  K. At the very initial stage ( $T > 820$  K, at the vicinity of  $T_1$ ), both Z-17.5Pd3-A and Z-17.5Pd3-V follow almost the same cooling rate, so that their cooling curves and those of the other samples almost coincide among another. Our measurement reveals the cooling rate of  $2.9 \times 10^3$  K/s for the first 20 ms. This cooling rate at very initial stage, however, seems not to give a significant influence to the overall cooling behavior as well as to the final as-cast structure of samples. Instead, we notice that the final as-cast structure is affected particularly by cooling characteristic at the subsequent stage ( $T < 820$  K). The rationalization is proposed as follows (see also the schematic description in Fig. 1). Once the molten alloy is ejected from the quartz tube into the mold, its temperature will suddenly drop as it touches the mold wall (step (a)). Then, temperature decreases as time elapses and the sample state enters the SCL region, *i.e.* the temperature region between  $T_g$  and  $T_1$ , (step (b)). A decrease of temperature will be accompanied by a decrease in volume of sample. This, therefore, leads to a shrinkage phenomenon and creates a very thin cavity between the mold-wall and the sample. Meanwhile, the viscosity of sample is still sufficiently low to enable the sample in SCL state to flow and to fill the cavity space. Thus, there is a competition between the volume-shrinkage and the molten flow at this stage. The rate of volume-shrinkage is determined by

$$\dot{\varepsilon}_{\text{shrink}} = \left( \frac{d\varepsilon}{dt} \right) = \left( \frac{d\varepsilon}{dT} \right) \left( \frac{dT}{dt} \right) = \alpha_{\text{SCL}} \left( \frac{dT}{dt} \right), \quad (1)$$

where  $\alpha_{\text{SCL}}$ ,  $T$ ,  $t$  are linear thermal expansion coefficient in SCL state, temperature and time, respectively; and the flow-rate due to the viscous-flow is defined by

$$\dot{\varepsilon}_{\text{flow}} = \frac{\sigma_{\text{sample}}(y)}{3\eta}, \quad (2)$$

where  $\eta$  is viscosity and  $\sigma_{\text{sample}}$  is uniaxial stress which can be estimated by the sample weight per unit area as a function of the distance from the upper part of the sample,  $y$ . Finally, the competition will stop and a permanent cavity starts to form when viscosity becomes too high to enable the flow due to the continuous decrease of temperature (step (c)).

The subsequent cooling characteristic then depends on the condition of the cavity. The gas used as the casting atmosphere may exist in the cavity and, in turn, acts as a heat-transfer medium during the subsequent cooling process. In the Z-17.5Pd3-A casting, the cavity is occupied by Ar gas. At atmospheric pressure, Ar gas is effective enough to transfer heat so that a smooth curve is exhibited during cooling process of this sample. On the other hand, almost nothing fills the cavity during casting Z-17.5Pd3-V, except air with an extremely low pressure ( $P \sim 2 \times 10^{-3}$  Pa). Thus, only a very small amount of gas molecules is responsible for the sample-to-mold heat transfer besides heat dissipation by radiation mode. Accordingly, after the formation of perma-

nent cavity (step (c) in Fig. 1), the cooling rate in Z-17.5Pd3V becomes much lower; this is represented by a deflection observed in the cooling curve. The deflection is then followed by a recalescence corresponding to the heat release during crystallization.

Experiment with Z-17.5Pd3-H and Z-17.5Pd3-1k is to check whether or not the gas species and pressure indeed affect the cooling characteristic of samples, particularly after the formation of the presumed cavity. Helium has a thermal conductivity almost 10 times higher than argon,<sup>14)</sup> while the Ar pressure applied during casting Z-17.5Pd3-1k is between those in casting Z-17.5Pd3-A and Z-17.5Pd3-V. As a result, the cooling curve of Z-17.5Pd3-H shows generally a higher cooling rate than that of Z-17.5Pd3-A, which agrees with the prediction. As the cooling curve is smooth without any recalescences, a glassy as-cast structure is also well confirmed by the corresponding XRD pattern in Fig. 2. Meanwhile, the cooling curve of Z-17.5Pd3-1k shows an almost the same cooling rate initially as in the other curves. A deflection to a lower cooling rate, however, is seen. This deflection neither leads to a recalescence, as shown in the cooling curve of Z-17.5Pd3-V, nor corresponds to early phase-decomposition<sup>15)</sup> since the XRD pattern confirms that Z-17.5Pd3-1k contains a glassy structure. The deflection observed is correlated with the sample-to-mold heat transfer effectiveness affected by the applied casting atmosphere. During the casting process of Z-17.5Pd3-1k, Ar gas which may exist in the cavity between the sample and the mold can still help this sample to undergo a high enough cooling rate to form glass during the subsequent cooling process, despite the low pressure of 1 kPa. However, since the number of Ar molecules is not as many as that in casting Z-17.5Pd3-A, the effectiveness of sample-to-mold heat transfer is also lower. Therefore, the cooling curve of Z-17.5Pd3-1k is not as smooth as that of Z-17.5Pd3-A, as it exhibits a deflection leading a slightly lower cooling rate before temperature continues to decrease to room temperature.

### 3.2 Analysis on the cooling curve by Newton's law of cooling

A temperature change of an object during cooling can be analyzed by the Newton's law of cooling, which is expressed mathematically by

$$\frac{dT}{dt} = -K(T - T_s), \quad (3)$$

where  $T$ ,  $T_s$  and  $K$  are temperature of the object at time  $t$ , temperature of the surrounding matter (mold) and an experimental cooling-constant, respectively. Plotting  $\ln(T - T_s)$  versus  $t$  therefore should give a straight line with slope  $-K$ , which means that the object is cooled by following a heat transfer mechanism with a constant parameter. We may use this law to analyze our cooling curves. Figure 3(a) shows the plots for the cooling curve of Z-17.5Pd3-1k, Z-17.5Pd3-A and Z-17.5Pd3-H in term of  $\ln(T - T_s)$  versus  $t$ . Here,  $T_s = 300$  K. The plots apparently do not result in a straight line and, thus, do not reveal a single value of  $K$  for each cooling curve. At the initial stage ( $T_1 > T > 820$  K), the plots almost coincide in one line, suggesting that the gradients  $-K_i$  are almost the same. At the subsequent stage ( $T \leq 820$  K), the

gradient  $-K_f$  for each curve becomes less steep than that in the initial stage and the value depends on the applied casting atmosphere. The plot of  $K$  versus casting atmosphere (inset in Fig. 3(a)) shows that varying the casting atmosphere does not give a remarkable change to the cooling-constant of the initial cooling process,  $K_i$ . On the other hand, the cooling-constant of the subsequent cooling process,  $K_f$ , apparently depends on the casting atmosphere. This means that sample-to-mold heat transfer for the whole cooling process is not only affected by a constant parameter, which is so far considered to be attributed to material of the mold, *i.e.* copper. Heat transfer accommodated mainly by the copper-mold is suggested to occur only at the initial stage of cooling process, in which  $K$  value is almost the same for all curves plotted. During the subsequent stage, gas used as the casting atmosphere will give a significant effect on sample-to-mold heat transfer.

Cooling characteristic of the subsequent stage will depend on the species and pressure of gas applied as the atmosphere. Fig. 3(b) demonstrates that  $K_f$  rises significantly when He is used as the casting atmosphere instead of Ar, whose thermal conductivity  $\lambda$  is only about a tenth of He's. For a given casting atmosphere, say Ar, increasing pressure will raise  $K_f$  (Fig. 3(c)). This analysis agrees with our experimental result in which the cooling rate becomes higher for Z-17.5Pd3-1k, Z-17.5Pd3-A and Z-17.5Pd3-H, successively.

### 3.3 Deflection in the cooling curve

The deflection in the cooling curve, representing a deviation in cooling characteristic between the initial and subsequent stage, is clearly observed at temperature around 820 K, *i.e.*  $T_g + 160$  K (see Fig. 1 or Fig. 3(a)). This deflection actually corresponds to the formation of the cavity during cooling in which the condition affects the cooling characteristic of sample, particularly at the subsequent cooling stage. By using eqs. (1) and (2), we may calculate temperature at which the curve deflects and compare with the experimental result.

From the cooling curves, we obtain that the average cooling rate prior to the deflection is about  $2.3 \times 10^3$  K/s. Our actual measurement by a dilatometry revealed that the linear thermal expansion coefficient of this alloy in the glassy state is  $1.6 \times 10^{-5}$  K<sup>-1</sup>. For the SCL state, it can be concluded empirically based on experimental results of thermal expansion measurement for Pd- and Zr-based glassy alloys<sup>16,17</sup> that the value is generally about twice as that of the glassy state, thus  $3.2 \times 10^{-5}$  K<sup>-1</sup>. Therefore, the shrinkage-rate is  $\dot{\epsilon}_{\text{shrink}} = |(-3.2 \times 10^{-5} \text{ K}^{-1})(2.3 \times 10^3 \text{ K s}^{-1})| = 7.4 \times 10^{-2} \text{ s}^{-1}$ . The permanent cavity begins to form when the competition between the volume-shrinkage and the molten-flow stops and the shrinkage starts to become dominant; thus, when  $\dot{\epsilon}_{\text{flow}} = \dot{\epsilon}_{\text{shrink}}$ , *i.e.* when  $\eta = \sigma_{\text{sample}} / 3(7.4 \times 10^{-2} \text{ s}^{-1})$ .  $\sigma_{\text{sample}}$  depends on the position in the sample,  $y$ , measured longitudinally from the upper part, but here, it is calculated for the case of the bottom part of the sample, where the thermocouple was placed to record the cooling curve. At the bottom of sample,  $y = L$ , where  $L$  is the sample's length. Accordingly,  $\sigma_{\text{sample}} = \rho \cdot L \cdot g$ , where  $\rho$  and  $g$  are the sample density and acceleration of gravity, respectively. Therefore, we can obtain the viscosity of sample when

the cavity starts to develop permanently and the deflection in the cooling curve takes place, *i.e.*  $\eta = (6.5 \times 10^3 \text{ kg}\cdot\text{m}^{-3})(5 \times 10^{-2} \text{ m})(10 \text{ m}\cdot\text{s}^{-2}) / 3(7.4 \times 10^{-2} \text{ s}^{-1}) = 1.5 \times 10^4 \text{ Pa}\cdot\text{s}$ . To correlate this viscosity value to temperature, one may use the fragility plot of an SCL state, in which the viscosity is plotted as a function of temperature. Since there is no specific report regarding the fragility plot of the present alloy, we adopted data for another glass-forming alloy in Zr-based system for comparison. Masuhr *et al.* have reported a comprehensive viscosity measurement in a Zr-Ti-Cu-Ni-Be glass-forming alloy and applied the Cohen-Grest (CG) model to fit the  $(T-\eta)$ -correlation in the fragility plot.<sup>18</sup> For the Zr-Ti-Cu-Ni-Be alloy, the viscosity of  $1.5 \times 10^4 \text{ Pa}\cdot\text{s}$  corresponds to temperature of 793 K which is about 170 K higher than its glass transition temperature ( $T_g$ ). This calculation, therefore, compares well with our experimental result in which the deflection in the cooling curve is observed at a temperature of  $T_g + 160$  K.

### 3.4 Explanation on the origin of variation in as-cast structure

Now, there actually remains one important question why the present alloy especially shows the remarkable dependence of as-cast structure on the casting atmosphere. In fact, we also actually found that there are some alloys in Zr-Al-Ni-Cu-Pd system in which the as-cast structure does not depend so much on the casting atmosphere, *e.g.* the Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Cu<sub>17.5</sub> alloy.<sup>19</sup> In this alloy, the as-cast structure (for a given diameter of rod sample) does not change and the critical diameter of glass formation ( $d_c$ ) remains 6 mm even though the pressure of Ar as the casting atmosphere is varied from vacuum to atmospheric one. The dependence of cooling characteristic on the casting atmosphere during mold-casting, however, is similar as what observed in the case of the Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Pd<sub>17.5</sub> alloy, *i.e.* the cooling characteristic depends strongly on the casting atmosphere particularly starting at a temperature around  $T_g + 160$  K. Thus, here we can notice that in mold-casting process of Zr-Al-Ni-Cu-Pd system, the casting atmosphere influences significantly the cooling characteristic particularly at low-temperature side of SCL region. Nevertheless, whether or not it will lead to a variation in as-cast structure seems to depend on the composition.

One may suggest that the phenomenon in which the as-cast structure varies with the change of casting atmosphere, may originate from the effect of pressure on nucleation behavior. But, it should be emphasized that the order of pressure applied in this work is low to give such a effect, despite the wide range of pressure from vacuum to atmospheric one. Our calculation reveals that the effect of a pressure of  $10^5$  Pa (atmospheric one) on the change of activation energy for nucleation is 100,000 times lower than that of the free-energy difference between the SCL and crystalline phase in the Zr-Al-Ni-Cu-Pd alloy system. Therefore, we cannot expect that varying pressure ranging from vacuum to atmospheric one may lead to a shift of crystallization curve in the T-T diagram of the present alloy and, thus, the obtained as-cast structure will vary accordingly, as what suggested previously in the work of Kato *et al.*<sup>12,13</sup>

Explanation on the origin of variation in as-cast structure

of the present alloy due to the change of casting atmosphere pressure is then rationalized as follows. The  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy has nano-size spherical QC particles with a high precipitation density as the primary phase during devitrification. Saida *et al.*<sup>20)</sup> reported that nucleation-rate and growth-rate at the onset temperature of the primary quasi-crystallization in the  $Zr_{65}Al_{7.5}Ni_{10}Cu_{17-x}Pd_x$  system respectively increases and decreases with increasing Pd content  $x$ . For the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy, the nucleation-rate and growth-rate are, respectively, about  $10^6$  times larger than and  $1/15$  of those of  $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$  in which micro-size of fcc- $Zr_2Ni$  particles precipitates as the primary phase. Therefore, one can fairly expect that the quasi-crystallization in the Zr-Al-Ni-Cu-Pd alloys occurs at a low-temperature side of the SCL region, where the nucleation rate is higher and the growth rate is lower than those at the high-temperature side. Janlewing and Koester<sup>21)</sup> evaluated a T-T-T diagram for the primary quasicrystallization in  $Zr_{64.5}Al_{7.5}Ni_{11}Cu_{12}Hf_5$  and  $Zr_{69.5}Al_{7.5}Ni_{11}Cu_{12}$  alloys, and concluded that the nose position, characterizing a border-curve between SCL and crystalline phase, of these T-T-T curves were situated just about 100 K higher than  $T_g$ . This strongly supports the idea that the T-T-T curve of the primary quasicrystallization in the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  also is located at a very low-temperature side of the SCL region. The location of this T-T-T curve, therefore, possibly coincides with the variation of cooling characteristic due to the change of atmosphere in mold-casting process for the same casting diameter (Fig. 4). Accordingly, the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy shows different as-cast structures with the variation of atmosphere-gas species or pressure applied during mold-casting process.

As the permanent cavity formed at the low-temperature side of the SCL region is expected to be larger with increasing casting diameter, the cooling behavior of samples in the SCL region with a larger casting diameter depends more remarkably on the casting atmosphere. Accordingly, one can expect an improvement in critical diameter ( $d_c$ ) of single-glassy rod sample for an alloy of which T-T-T curve of the primary quasi-crystallization is located at a low temperature side in the SCL region, *e.g.* the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy, by either increasing pressure of a given casting-atmosphere gas or using a gas with higher thermal conductivity during sample fabrication with mold-casting technique. The applied gas species, of course, should not generate other chemical reactions during casting process, *e.g.* by using the noble gas. Figure 5 shows the XRD patterns of as-cast structure of the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  rod samples cast under atmospheric pressure of argon or helium with various diameters. The result reveals that the critical diameter of the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  is successfully improved from 5 mm to 7 mm by replacing argon with helium as the casting atmosphere. Applying helium instead of argon as the casting atmosphere, however, does not give a significant improvement in the critical diameter of the  $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$  glassy samples;<sup>19)</sup>  $d_c$  of this alloy remains about 6 mm regardless of the applied casting atmosphere. This indicates that the T-T-T curve of the  $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$  alloy is located at a high temperature side in the SCL region (see Fig. 4), which is contrary to that of the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy, so that the

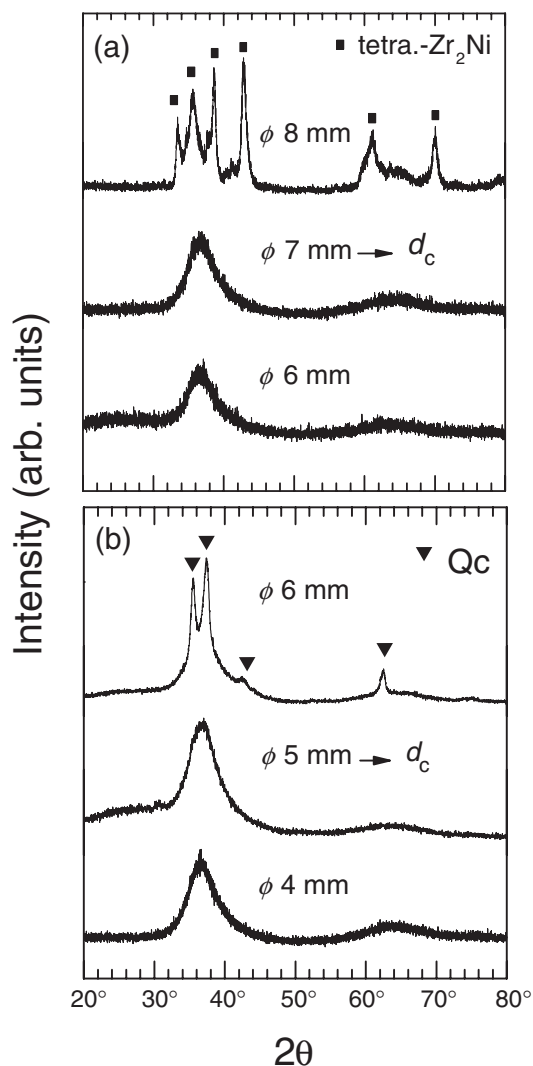


Fig. 5 X-ray diffraction patterns of the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy of various diameter cast under atmospheric pressure ( $10^5$  Pa) of (a) He, or (b) Ar showing a different critical diameter ( $d_c$ ) of glassy rod-sample due to the change in gas species used as the casting atmosphere.

deviation of cooling characteristic due to the variation of casting atmosphere does not give a remarkable effect on the as-cast structure. The as-cast structure of such an alloy is, thus, only affected by the initial cooling behavior which is, in this case, determined by casting diameter.

#### 4. Conclusions

We have proposed an explanation on the origin of the remarkable effect of mold-casting chamber atmosphere on as-cast structure in  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  bulk glassy or nano-quasicrystal-forming alloy. The  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  rod samples exhibit different cooling characteristics as various atmospheres are applied in the chamber during casting. It is found that the different cooling characteristics are due to the variation of gas species and pressure existing in the cavity presumably formed during the sample cooling process, which affect sample-to-mold heat transfer. A deflection is found in the cooling curve at a low-temperature side of the super-cooled-liquid (SCL) region, *i.e.*  $T = T_g + 160$  K. The de-

deflection reflects a deviation of heat transfer mechanism along the cooling process of the sample: at the initial stage prior to the deflection, heat transfer is attributed mainly to the copper mold, while at the subsequent stage beyond the deflection, the sample-to-mold heat transfer is affected significantly by the gas species and pressure applied during casting. Variation in cooling characteristic due to the change of gas species or pressure in casting atmosphere, therefore, is only remarkable at the low-temperature side of the SCL region. Meanwhile, the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy is considered to have a time-temperature-transformation (T-T-T) curve of primary quasicrystallization situated at the same region. This coincidence is then regarded as the origin of variation in as-cast structure of the  $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$  alloy with the change of casting atmosphere. Results of this work also implies that, even in the sample preparation by a mold-casting technique, the critical diameter of a bulk glass-forming alloy, particularly whose T-T-T curve of the primary crystallization is located at a low-temperature side of the SCL region, can be improved by applying a noble gas with high thermal conductivity or pressure as a casting atmosphere. Moreover, by utilizing the cooling characteristic of a glass-forming alloy under an atmosphere-controlled casting process, one may also expect to obtain, for example, a nanocrystal-/nanoquasicrystal-dispersed metallic glassy phase in as-cast state which is a solution for the absent plasticity in monolithic glasses.

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