Solidification Analyses of Bulky $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ Glass Produced by Casting into Wedge-Shape Copper Mold

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The liquid-crystalline transformation behavior during continuous cooling and the transformation-induced structure were examined for a $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ molten alloy which was ejected into a wedge-shape cavity in a copper mold. The wedge-shape cavity has a constant depth of 50 mm and different vertical angles (θ) ranging from 5 to 15 degrees. The ejection temperature of the molten alloy was also changed in the range of 1273 to 1573 K. The cast structure consists only of a glassy phase in the θ range smaller than 10 degrees and changes to a mixed structure consisting of glassy and nonequilibrium crystalline Zr_2Ni and Zr_2Cu phases in the higher θ range. The glass transition temperature and crystallization temperature of the cast metal glass are 683 and 778 K, respectively, which agree with those for the melt-spun glassy ribbon. The start (Cs) and termination (Ct) points for the transformation from the supercooled liquid to crystalline phases during continuous cooling were determined from the thermal analytical data obtained at different sites in the wedge-shape cavity and the continuous-cooling-transformation (C.C.T.) curves were constructed. The nose temperature (T_n) and the time (t_n) up to the nose point in the C.C.T. curves were 1018 K and 0.93 s respectively. The critical cooling rate for glass formation defined by $(T_m - T_n)/t_n$ is evaluated to be 110 K/s. Further, the time interval between Cs and Ct is as short as 0.2 s and the fast growth reaction is attributed to the easy formation of the nonequilibrium crystalline phases and the increase in temperature caused by the precipitation-induced recalescence.

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I. Introduction

Recently, amorphous alloys with a wide supercooled liquid region above 80 K before crystallization have been obtained in a number of alloy systems such as Ln-Al-TM⁽¹⁾⁽²⁾, Mg-Ln-TM⁽³⁾⁽⁴⁾, Zr-Al-TM⁽⁵⁾⁽⁶⁾, Ti-Zr-TM⁽⁷⁾ and Ti-Zr-Be-TM⁽⁸⁾ (Ln=lanthanide metal, TM=transition metal). Subsequently, these amorphous alloys have been produced as a bulk form with a maximum thickness reaching about 25 mm by various conventional solidification methods such as water quenching⁽⁹⁾, arc melting⁽¹⁰⁾, copper mold casting⁽¹¹⁾, high-pressure die casting⁽¹²⁾ and unidirectional solidification⁽¹³⁾. These amorphous alloys with large glass-forming ability have been named as metal glasses similar to oxide glasses, on the basis of the significant distinction in the glass-forming ability between the new amorphous alloys and the previously reported amorphous alloys with a much narrow supercooled liquid region and without glass transition. More recently, we have carried out a series of studies on the construction of continuous-cooling-transformation (C.C.T.) curve and the determination of the critical cooling rate for glass formation for the above-described metal glasses with large glass-forming ability. It has al-

ready been reported⁽¹⁴⁾ that the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{12}\text{Cu}_{18}$ glasses have lower critical cooling rates for glass formation of the order 10 to 20 K/s from the C.C.T. curves obtained through the measurement of the cooling rate and transformation behavior of their molten alloys on a copper hearth in an arc furnace. The critical cooling rate of their molten alloys prepared by arc melting is strongly dependent on the number of cycles for melting. That is, the critical cooling rate decreases significantly by the repetition of arc melting up to about seven times and becomes saturated to a minimum value of the order 10 to 20 K/s after about ten times. This significant change in the critical cooling rate has been thought to originate from the elimination of heterogeneous nucleation sites through the increase in the purity of the molten alloy. This result also suggests that the critical cooling rate including the influence of heterogeneous nucleation is strongly dependent on the measurement method. Bulky metal glasses with diameters above 5 mm have easily been produced for the Zr-based alloys by a copper mold casting method⁽¹⁵⁾. Consequently, it is important for the Zr-based glasses to construct the C.C.T. curve in the copper mold casting process and to determine the critical cooling rate for glass formation. This paper is intended to examine the transformation behavior during continuous cooling and solidification structure at different cavity sites for the molten $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy which was cast into wedge-

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shape copper molds and to determine the critical cooling rate for glass formation through the construction of the C.C.T. curve.

II. Experimental Procedure

A $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy was chosen in the present study because it had a large glass-forming ability through the suppression of heterogeneous nucleation⁽¹³⁾. The mother alloy was prepared by arc melting a mixture of pure each metal in an argon atmosphere. Figure 1 shows a schematic illustration of the equipment which was used for the solidification analyses of the Zr-Al-Ni-Cu-Pd alloy. The wedge-shape cavity in the copper mold has the depth of 50 mm and vertical angles between 5 and 15 degrees. The ejection pressure of the molten alloy was fixed to be 0.05 MPa while the ejection temperature was changed in the range of 1273 to 1573 K. The cooling rates of the ejected melt were measured with Pt-PtRh thermocouples at five different sites along the depth direction in the wedge-shape cavity shown in Fig. 1. The solidification structure of the wedge-shape ingot was examined by X-ray diffractometry and optical and transmission electron microscopy (OM and TEM). The OM sample was etched for 5 s at 298 K in a solution of 1% fluoric acid aqueous solution and the TEM sample was prepared by thinning electrolytically at about 230 K in a solution of 10% nitric acid and 90% methanol. The thermal stability associated with glass transition, supercooled liquid and crystallization was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Thermal analyses to determine the liquid and solid temperatures

were also made by differential thermal analysis (DTA) at different scanning rates of 0.03 to 3.03 K/s.

III. Results

Figure 2 shows the relation between the depth from the vertical point of the wedge-shape cavity (d) and the vertical angle (θ) for the formation of an amorphous phase at an ejection temperature of 1473 K. The amorphous phase is obtained over the whole depth range in the θ range smaller than 10 degrees. However, no amorphous single phase is formed in the larger θ range and the maximum depth for formation of an amorphous single phase (d_c) decreases to about 30 mm at $\theta=12.5$ degrees and 20 mm at $\theta=15$ degrees. Figure 3 also shows the change in the d_c value at $\theta=12.5$ degrees with ejection temperature. The d_c value tends to increase with increasing ejection temperature, i.e., from 24 mm at 1273 K to 30 mm at 1573 K. As examples, Fig. 4 shows the optical micro-

Fig. 1 Schematic illustration of an equipment used for the preparation of a wedge-shape cast sample and the measurement of continuous-cooling-transformation (C.C.T.) behavior at different sites in the transverse cross section.

Fig. 2 Change in the critical distance (d_c) from the vertical point for the formation of a glassy phase as a function of vertical angle (θ) for a $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy which was cast into the wedge-shape copper mold from a temperature of 1473 K.

Fig. 3 Change in d_c as a function of ejection temperature of molten alloy for a $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy which was cast into the wedge-shape mold with θ of 12.5 degrees.

Fig. 4 Optical micrographs taken from the regions (a and b) in the transverse cross section of the cast $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy with the wedge shape of $\theta = 12.5$ degrees.

graphs at the sites marked with a and b in the transverse cross section. It is clearly seen that the transition from glassy to crystalline phase takes place with an increase of the distance from the vertical edge or the surface contacted with the copper mold. In order to confirm the formation of the amorphous phase and to identify the crystalline phase, the X-ray diffraction patterns were taken from the regions A, B and C in the transverse cross section. As shown in Fig. 5, the X-ray diffraction patterns are identified to be an amorphous single phase for the region C, amorphous plus bct- Zr_2Ni plus bct- Zr_2Cu phases for the region B and Zr_2Cu plus Zr_2Ni phases for the region A. The crystallites with a particle size of 0.4 to 5 μm shown in Fig. 4 are concluded to consist of Zr_2Ni and Zr_2Cu phases. Considering that the equilibrium structure in the Zr-Al-Ni-Cu-Pd alloy consists of Zr_2Ni , Zr_2Cu , Zr_2Al and Zr_2Pd phases⁽¹³⁾, it is said that the regions A and B have the nonequilibrium crystalline structure. The formation of the nonequilibrium $\text{Zr}_2(\text{Ni}, \text{Al}, \text{Pd})$ and $\text{Zr}_2(\text{Cu}, \text{Al}, \text{Pd})$ phases in the region A indicates the difficulty of the transition from the supercooled

Fig. 5 X-ray diffraction patterns taken from the regions A, B and C in the transverse cross section of the cast $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy with the edge shape of $\theta = 12.5$ degrees.

Fig. 6 Bright-field electron micrograph and selected-area electron diffraction pattern taken from the region C of the cast $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy with the wedge shape of $\theta = 12.5$ degrees.

liquid to equilibrium multiple phases which is an important factor for the achievement of large glass-forming ability.

The absence of crystallinity in the amorphous phase formed in the region C was also examined by TEM. Figure 6 shows a bright-field electron micrograph and selected-area electron diffraction pattern of the cast Zr-Al-Ni-Cu-Pd alloy taken from the site which is away by about 10 mm from the vertical point. The bright-field image shows only featureless contrast and the diffraction pattern also consists of halo rings, indicating clearly the formation of an amorphous single phase. Figure 7 shows the DSC curve of the cast alloy which was taken from the same region as the TEM sample. One can see a very broad exothermic reaction due to structural relaxation in the temperature range below about 680 K, followed by an endothermic reaction due to the glass transition around 683 K, the appearance of a wide supercooled liquid region in the range of 683 to 778 K, and then a sharp exothermic reaction due to crystallization with the onset temperature at 778 K. The glass transition temperature (T_g) and the temperature interval of supercooled liquid

Fig. 7 DSC curve taken from the region C of the cast $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy with the wedge shape of $\theta=12.5$ degrees.

Fig. 8 Temperature-time curves at different sites (a) to (e) in the transverse cross section of the cast $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy with the wedge shape of $\theta=12.5$ degrees. T_g , T_x and eutectic temperature (T_e) are also shown for reference.

region defined by the difference between T_g and onset temperature of crystallization (T_x), $\Delta T_x (=T_x - T_g)$ of the cast alloy are just the same as those ($T_g=683$ K, $\Delta T_x=95$ K) for the melt-spun amorphous ribbon with the same alloy composition. The agreement suggests that there is no distinct difference in the disordered structure between the cast ingot and the melt-spun ribbon.

We have tried to construct the C.C.T. curve of the $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ molten alloy by examining the transformation behavior during continuous cooling at different sites in the transverse cross section. Figure 8 shows the transformation behavior of the melt during continuous cooling at the sites which are away by 10 mm (a), 20 mm (b), 30 mm (c), 35 mm (d) and 40 mm (e) from the vertical point of the wedge-shape cavity, together with

Fig. 9 Differential thermal analytical curves measured at differential cooling rates for a $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy.

Fig. 10 Continuous-cooling-transformation (C.C.T.) curves for the transformation from supercooled liquid to crystalline phases for a $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15}\text{Pd}_5$ alloy. The Cs and Ct represent the start and termination points of the transformation, respectively.

the data of eutectic temperature (T_e), T_g and T_x . Based on the DSC data at a low cooling rate of 0.033 K/s shown in Fig. 9, it is confirmed that the present alloy is located near the eutectic point and the temperature difference between the precipitation temperature of a primary crystalline phase and the eutectic temperature is as small as 33 K. No appreciable recalescence phenomenon is seen in the curves (a) and (b) shown in Fig. 8, indicating the formation of a mostly single amorphous phase at the sites which are away by 10 and 20 mm. However, a slight recalescence is seen at 1040 K in the curve (c) and the temperature at which the recalescence begins to occur and

the amount of the recalescence increase with increasing distance from the vertical point. Based on the thermal analytical data at different cooling rates shown in Fig. 8, the C.C.T. curves from the supercooled liquid to crystalline phases for the Zr–Al–Ni–Cu–Pd alloy are shown in Fig. 10, where the Cs and Ct represent the start and termination points of the transformation, respectively. From the C.C.T. curves, the nose temperature (T_n) for the start of the transformation is measured to be 1023 K and the critical cooling rate for glass formation defined by $(T_m - T_n)/t_n$ is evaluated to be 110 K/s. Here, T_m is the melting temperature and t_n is the time up to the start of the transformation at T_n . It is further seen that this alloy has a high reduced glass transition temperature (T_g/T_m) of 0.61. Here, it is important to point out that the time interval between Cs and Ct is as short as about 0.2 s and hence the growth of the nonequilibrium crystalline phases of $Zr_2(Ni, Al, Pd)$ and $Zr_2(Cu, Al, Pd)$ proceeds at rather high velocities. A more detailed discussion on this point is described later.

IV. Discussion

1. Reason for the difference in the critical cooling rate between the present casting method and the previous arc-melted method

It is shown in Section III that the critical cooling rate for the formation of amorphous phase in the $Zr_{60}Al_{10}Ni_{10}Cu_{15}Pd_5$ alloy is measured to be about 110 K/s from the C.C.T. curve. The critical cooling rate is larger by about one order than those (10 to 20 K/s) of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{60}Al_{10}Ni_{12}Cu_{18}$ alloys without Pd. Little is known about the influence of Pd on the glass-forming ability of the Zr–Al–Ni–Cu alloy. However, it is difficult to consider that the dissolution of Pd causes the significant decrease in the glass-forming ability, because the addition of Pd has been reported⁽¹³⁾ to cause an easy formation of bulky metal glasses by a unidirectional solidification method. Additionally, the effect of the addition of Pd has been attributed to the suppression of heterogeneous nucleation of a crystalline phase in the supercooled liquid. Consequently, the significant increase in the critical cooling rate for the Pd-containing alloy in comparison with those for the Zr–Al–Ni–Cu alloys is presumably due to the difference in the methods used for the construction of the C.C.T. curves. It has been pointed out⁽¹³⁾ that the critical cooling rate obtained by the arc melting method is strongly dependent on the number (N) of cycles of melting. That is, the critical cooling rate is about 100 K/s for $N=3$ and decreases significantly to about 10 K/s for $N=7$. This distinct change suggests that the repetition of melting causes the increase in the cleanness of the molten alloy through the elimination of the source of heterogeneous nucleation. On the other hand, the melt in the present measurement method was once melted in a quartz tube and ejected into the wedge-shape copper mold. In this procedure, it is difficult to maintain a high degree of cleanness for the

melt, even in the case where the arc-melted alloy prepared by the repetition above seven times is used as a mother alloy. This difficulty seems to be the reason for the increase in the critical cooling rate for glass formation by about one order in the present measurement method. Furthermore, this distinct difference also indicates the possibility that the improvement of the degree of cleanness for the melt causes the achievement of the critical cooling rate which is of the order 10 K/s even by the wedge-shape casting method.

2. Reason for the fast growth reaction of the nonequilibrium crystalline phases from supercooled liquid

The C.C.T. curves shown in Fig. 10 indicate clearly that the transformation from the supercooled liquid to the crystalline phases takes place very rapidly after the generation of crystalline nuclei. Considering that the crystallites in the region A consist of nonequilibrium bct- $Zr_2(Ni, Al, Pd)$ and bct- $Zr_2(Cu, Al, Pd)$ phases, the formation of the nonequilibrium crystalline phases as an intermediate-stage phase seems to enable the fast growth reaction. In addition, the increase of temperature due to the recalescence resulting from the precipitation of their crystalline phases seems to play an important role in the acceleration of the growth reaction. The fast growth reaction also implies that the retardation of the transformation from supercooled liquid to crystalline phases is due to the difficulty of the generation of crystalline nuclei. This result is consistent with the previously reported concept⁽¹⁶⁾⁽¹⁷⁾ for the achievement of the large glass-forming ability for the present amorphous alloys. That is, the main reason for the large glass-forming ability has been attributed to the difficulty of nucleation reaction of a crystalline phase resulting from the increase in solid/liquid interfacial energy in the highly dense random packed liquid consisting of more than three kinds of elements with significantly different atomic sizes. This result also suggests that an alloy design leading to the retardation of the growth reaction enables a further increase in the glass-forming ability.

V. Summary

The $Zr_{60}Al_{10}Ni_{10}Cu_{15}Pd_5$ molten alloy was cast into a wedge-shape cavity with a depth of 50 mm and different vertical angles (θ) of 5 to 15 degrees in a copper mold and the transformation behavior during continuous cooling at different sites and the solidification structure were examined by thermal analyses and conventional metallographic techniques. The results obtained are summarized as follows:

(1) The cast ingot consists only of a glassy phase in the θ range smaller than 10 degrees and the further increase in θ causes the formation of coexistent glassy and crystalline phases.

(2) The crystalline phase consists of nonequilibrium $Zr_2(Ni, Al, Pd)$ and $Zr_2(Cu, Al, Pd)$ phases with particle sizes of 0.4 to 5 μm .

(3) The cast metal glass shows the sequent phase transition of glassy solid $\rightarrow$ supercooled liquid $\rightarrow$ crystalline phase upon continuous heating and the T_g and T_x values are 683 and 778 K, respectively, in agreement with those for the corresponding melt-spun glassy ribbon.

(4) Based on the thermal analytical data, the C.C.T. curves from the supercooled liquid to the intermediate crystalline phases were determined at the start (Cs) and termination (Ct) points. The nose temperature (T_n) and the time up to the nose point (t_n) in the C.C.T. curve were measured to be 1018 K and 0.93 s, respectively. The time interval between the Cs and Ct points is as short as 0.2 s and the growth reaction takes place rapidly. The easy growth reaction is presumably due to the precipitation of the intermediate crystalline phase and the increase of temperature caused by recalescence.

(5) The critical cooling rate for glass formation which was defined by $(T_m - T_n)/t_n$ was evaluated to be 110 K/s which was about one order larger than those obtained after the seven repetitions of melting by the arc-melted method for $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{12}\text{Cu}_{18}$ alloys. The significant difference is interpreted to result from the difference of the degree of the cleanness of the molten alloy which is related to the ease of heterogeneous nucleation of crystalline phase. It is concluded, therefore, that a further improvement of the cleanness of the molten alloy causes a further increase in the glass-forming ability.

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