High Strength Bulk Amorphous Alloys with Low Critical Cooling Rates (*Overview*)

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This paper aims to review our recent research results on new amorphous alloys. The main topics consist of the following five parts; (1) the finding of new amorphous alloys with extremely large glass-forming ability in a number of alloy systems, (2) the mechanism for the achievement of the large glass-forming ability, (3) the clarification of fundamental properties of the new amorphous alloys, (4) the successful examples of producing bulk amorphous alloys by four different techniques of water quenching, metallic mold casting, arc melting and unidirectional zone melting, and (5) the high tensile strength of the bulk amorphous alloys. These new results enable the elimination of the limitation of sample shape which has prevented the development of amorphous alloys as engineering materials and are expected to give rise to the revisit age to amorphous alloys.

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I. Introduction

Since the first success of preparing an amorphous phase in the Au-Si system by rapid solidification in 1960⁽¹⁾, a great number of scientific and engineering data for amorphous alloys have been accumulated up to date. As a result, it has been clarified that amorphous alloys have the features of new alloy compositions and new atomic configurations which are different from those for crystalline alloys. These features enable the appearance of various kinds of characteristics such as good mechanical properties, useful physical properties and unique chemical properties⁽²⁾⁻⁽⁵⁾ which have not been obtained for conventional crystalline alloys. More recently, amorphous alloys have also attracted increasing interest as a precursor to produce nanocrystalline alloys by crystallization because of the appearance of good mechanical properties⁽⁶⁾⁽⁷⁾, soft magnetism⁽⁸⁾⁽⁹⁾, hard magnetism⁽¹⁰⁾⁽¹¹⁾, high magnetostriction in low applied fields⁽¹²⁾, and high catalytic properties⁽¹³⁾ which have not been obtained for amorphous or crystalline single phase alloys. Based on these research results, the scientific and engineering importance of the amorphous and nanocrystalline alloys has increased significantly for the last three decades. However, very little is known about the formation and properties of amorphous alloys where the supercooled liquid region defined by the temperature difference between crystallization temperature (T_x) and glass transition temperature (T_g), $\Delta T_x (= T_x - T_g)$, exceeds 80 K, even though some data on Pd- and Pt-based amorphous alloys with the supercooled liquid region reaching about 70 K have been presented⁽¹⁴⁾⁽¹⁵⁾. This paper is intended to review our recent results on the fabrication and fundamental properties of the new amorphous alloys with ΔT_x values larger than 80 K which were obtained by the present author's

group for the last five years.

II. History of Amorphous Alloys with Large Glass-Forming Ability and Its Dominant Factors

It is essential for the formation of an amorphous phase by rapid solidification to suppress the nucleation and growth reaction of a crystalline phase in the supercooled liquid region between melting temperature (T_m) and T_g . The minimum critical cooling rate for glass formation (R_c) has been reported⁽¹⁶⁾ to be above 10^4 K/s for Fe-, Co- and Ni-based amorphous alloys and above 10^2 K/s for Pd- and Pt-based amorphous alloys, being much higher than those for oxide glasses. More recently, we have succeeded in finding new ternary amorphous alloys in the Mg-TM-Ln⁽¹⁷⁾⁻⁽¹⁹⁾, Ln-Al-TM⁽²⁰⁾⁽²¹⁾, Zr-Al-TM⁽²²⁾⁽²³⁾, Hf-Al-TM⁽²⁴⁾ and Ti-Zr-TM⁽²⁵⁾ systems where the critical cooling rates for glass formation range from 10 to 100 K/s, as shown in Fig. 1. It is seen that these ternary amorphous alloys have higher reduced glass transition temperature (T_g/T_m) as compared with those for previously reported amorphous alloys. Furthermore, Fig. 2 shows that these ternary amorphous alloys have larger ΔT_x values. There is a clear tendency for R_c to decrease with increasing ΔT_x . These results allow us to conclude that the large glass-forming ability is obtained in the simultaneous satisfaction of high T_g/T_m and large ΔT_x .

Various models to describe the glass formation and glass-forming ability have been proposed up to date⁽¹⁶⁾. These models can be grouped into three categories of thermodynamics, kinetics and structure, depending on the factors that are viewed as decisive in the formation of amorphous alloys. Therefore, the reason why the above-described ternary amorphous alloys have lower critical cooling rates for glass formation must be consistently understood based on the three factors. Firstly, we inves-

Fig. 1 Relation between the minimum critical cooling rate for glass formation (R_c) and the reduced glass transition temperature (T_g/T_m) for new ternary amorphous alloys in the Ln-Al-TM, Zr-Al-TM and Mg-TM-Ln systems. The data of previously reported metallic amorphous alloys and oxide glasses are also shown for comparison.

Fig. 2 Relation between R_c and the temperature interval of supercooled liquid region $\Delta T_x (= T_x - T_g)$ for the new ternary amorphous alloys. The data on previously reported amorphous alloys are also shown for comparison.

tigate the reason for the large glass-forming ability from the thermodynamical point of view. It is generally known that the large glass-forming ability is obtained in the condition of low free energy $\Delta G(T)$ for the transformation of liquid to crystalline phase. In the relation of $\Delta G = \Delta H_f - T\Delta S_f$ for Gibbs free energy, the low ΔG value is obtained in the cases of low ΔH_f and large ΔS_f . Here, the ΔH_f and ΔS_f are enthalpy of fusion and entropy of fusion, respectively. The large ΔS_f is expected to

be obtained in multicomponent alloy systems because ΔS_f is proportional to the number of microscopic states. The free energy at a constant temperature also decreases in the cases of low chemical potential caused by the low enthalpy and high reduced glass transition temperature as well as of large interface energy between liquid and solid phases. Based on these thermodynamical aspects, it is concluded that the multiplication of alloy components leading to the increase in ΔS_f causes the increase in the degree of dense random packing which is favorable for the decrease in ΔH_f and the increase in solid/liquid interface energy. This interpretation is consistent with the present result that the large glass-forming ability has been obtained for the above-described multicomponent systems containing more than the three elements.

Secondly, we investigate the reason for the large glass-forming ability from the kinetic point of view. The homogeneous nucleation and growth of a crystalline phase with a spherical morphology from supercooled liquid are known to be expressed by the following relations⁽²⁶⁾.

$$I = 10^{30} / \eta \cdot \exp [-b\alpha^3\beta / (T_i(1-T_i)^2)] \quad [\text{cm}^{-3} \text{s}^{-1}] \quad (1)$$

$$U = 10^2 f / \eta \cdot [1 - \exp (-\beta\Delta T_i / T_i(T/T_m))] \quad [\text{cm s}^{-1}] \quad (2)$$

Here, T_i is the reduced temperature (T/T_m), ΔT_i is the difference in temperature from T_m , b is a shape factor and $16\pi/3$ for a spherical nucleus, η is viscosity and f is the fraction of nucleus sites at the growth interface. α and β are dimensionless parameters related to the liquid/solid interface energy (σ), ΔH_f and ΔS_f can be expressed as $\alpha = (N_0 V)^{1/3} \sigma / \Delta H_f$ and $\beta = \Delta S_f / R$. Here, N_0 , V and R are Avogadro number, atomic volume and gas constant, respectively. In these relations, the important parameters are η , α and β . The increase in the three parameters causes the decrease in I and U values, leading to the increase in glass-forming ability. The increase in α and β also implies the increase in σ and ΔS_f and the decrease in ΔH_f , being consistent with the interpretation on the achievement of large glass-forming ability derived from the thermodynamical point of view. Furthermore, one can notice that η is closely related to the reduced glass transition temperature and $\alpha^3\beta$ reflects the thermal stability of the supercooled liquid. The importance of the $\alpha^3\beta$ parameter can be understood from the following two examples; (1) when the value of $\alpha^3\beta^{1/3}$ exceeds 0.9 unseeded liquid would not in practice crystallize at any cooling rate, and (2) when $\alpha^3\beta^{1/3}$ is below 0.25, the liquid would be impossible to suppress crystallization.

Furthermore, the reason for the large glass-forming ability of the ternary alloys was investigated from the structural point of view. As exemplified in Fig. 3, the present ternary amorphous alloys consist of the elements with significantly different atomic sizes and the atomic size ratios among the three constituent elements exceeds 10%. That is, the atomic sizes of the constituent elements in the present ternary amorphous alloys can be classified into the three groups of larger, intermediate and smaller. Such a significant difference in the atomic sizes is expect-

Fig. 3 Atomic radii of the constituent elements for the new ternary amorphous alloys.

ed to cause the increase of packing density in the super-cooled liquid which enables the achievement of a large liquid/solid interfacial energy. The formation of a higher degree of dense random packed structure has also been confirmed from the X-ray diffraction profiles obtained from the ternary La–Al–Ni⁽²⁷⁾, Mg–Cu–La⁽²⁸⁾ and Zr–Al–Ni⁽²⁹⁾ amorphous alloys. As exemplified for an amorphous La₅₅Al₂₅Ni₂₀ alloy in Fig. 4, neither any prepeak at the lower angle side nor any separation on the second

peak is seen in the X-ray interference functions⁽²⁷⁾. The feature of the X-ray interference functions is very analogous to that for a liquid phase, indicating that the ternary amorphous alloy has a homogeneously mixed atomic configuration corresponding to the formation of a highly dense random packed structure. We have also evaluated the changes in the atomic distances and coordination numbers among the constituent elements upon crystallization of the ternary amorphous alloys from the radial distribution function (RDF) data obtained by the anomalous X-ray scattering technique⁽²⁹⁾. As an example, Table 1 summarizes the atomic distances and coordination numbers of each atomic pair for an amorphous Zr₆₀Al₁₅Ni₂₅ alloy in as-quenched and crystallized states⁽²⁹⁾. Although no significant change in the coordination numbers of Ni–Zr and Zr–Zr pairs upon crystallization is recognized, one can notice the drastic change in Zr–Al atomic pair upon crystallization. This result indicates the necessity of atomic rearrangement of Al atoms around Zr atoms in the progress of crystallization. Based on the above-described results and discussion, Table 2 summarizes the reasons for the achievement of the large glass-forming ability of the present ternary amorphous alloys in the Ln-, Mg-, Zr-, Hf- and Ti-based systems. It is again confirmed that the present large glass-forming ability is attributed to the difficulty of the nucleation and growth reactions of a crystalline phase caused by the in-

Fig. 4 X-ray interference functions $Q_i(Q)$ of an amorphous La₅₅Al₂₅Ni₂₀ alloy in as-quenched state and an annealed state for 300 s at 510 K.

Table 1 Atomic distances (r) and coordination numbers (N) calculated from (a) the ordinary radial distribution function (RDF), and from the environmental RDFs for (b) Zr and (c) Ni in the as-quenched and annealed Zr₆₀Al₁₅Ni₂₅ amorphous alloys.

		r_1/nm	N_{ZrNi}	r_2/nm	N_{ZrZr}	N_{ZrAl}
As-quenched	(a)	0.267 ± 0.002	2.3 ± 0.2	0.317 ± 0.002	10.3 ± 0.7	-0.1 ± 0.9
	(b)	0.267 ± 0.002	2.1 ± 0.5			
	(c)	0.269 ± 0.002	2.3 ± 0.2			
Annealed for 120 s at 730 K	(a)	0.268 ± 0.002	2.5 ± 0.2	0.318 ± 0.002	8.9 ± 1.0	1.0 ± 0.8
	(b)	0.267 ± 0.002	2.3 ± 0.5			
	(c)	0.271 ± 0.002	2.4 ± 0.2			
Crystallized (Annealed for 180 ks at 730 K)	(a)	0.268 ± 0.002	3.0 ± 0.2	0.322 ± 0.002	8.2 ± 0.9	0.8 ± 0.7
	(b)	0.267 ± 0.002	3.0 ± 0.5			
	(c)	0.273 ± 0.002	2.3 ± 0.2			

Table 2 Summary of the reasons for the achievement of the large glass-forming ability for some ternary alloy systems such as Ln-Al-TM, Mg-Ln-TM and Zr-Al-TM, etc. (Ln=lanthanide metal, TM=transition metal).

The constituent elements have large negative heats of mixing and large atomic size ratios above 10%

Formation of amorphous phase with a higher degree of dense random packed structure

Increase of solid/liquid interfacial energy

Suppression of nucleation of crystalline phases

Difficulty of atomic rearrangement of the constituent elements on a long range scale

Suppression of crystal growth

crease in the packing density of the supercooled liquid resulting from the constituent elements with significantly different atomic sizes and large negative heats of mixing.

III. The Mechanism for Large Glass-Forming Ability and Crystallization Behavior

Figure 5 plots the T_g and T_x as a function of Al content for the amorphous $Zr_{65}Al_xCu_{35-x}$ alloys⁽³⁰⁾. Although T_g increases almost linearly with increasing Al content, T_x shows a maximum at 7.5 at%Al, indicating that the extension of the supercooled liquid region is dominated by the retardation of crystallization. This result indicates clearly

Fig. 5 Changes in T_g , T_x and ΔT_x for amorphous $Zr_{65}Al_xCu_{35-x}$ alloys with Al content.

that it is important to clarify the crystallization behavior from the highly supercooled liquid for the understanding of the origin of the high thermal stability of the present supercooled liquid. We have confirmed⁽³⁰⁾ that the crystallization is completed only by the precipitation of a metastable bct $Zr_2(Cu, Al)$ phase and the phase is independent of annealing temperature. The precipitation of the $Zr_2(Cu, Al)$ phase during isothermal annealing takes place through a single exothermic reaction. The incubation time (τ) for the precipitation of the crystalline phase was also measured at various annealing temperatures (T_a). Figure 6 shows the Arrhenius plot of the τ value for $Zr_{67}Cu_{33}$ binary and $Zr_{65}Al_{7.5}Cu_{27.5}$ and $Zr_{65}Al_{20}Cu_{15}$ ternary amorphous alloys. The deviation of τ to the positive side from the linear relation in the supercooled liquid region is seen only for the $Zr_{65}Al_{7.5}Cu_{27.5}$ alloy with the widest supercooled liquid region, indicating the suppression of the precipitation of the $Zr_2(Cu, Al)$ phase from the supercooled liquid. Similar deviation to the positive side in the supercooled liquid has also been recognized⁽³⁰⁾ for η which was evaluated from the relation of $\tau \propto T\eta/(T_m - T)^2 f^{(31)}$ for the amorphous $Zr_{65}Al_{7.5}Cu_{27.5}$ alloy. It is therefore said that the supercooled liquid of the Zr-Al-Cu alloy has a unique atomic configuration which causes the increase in η and the decrease in atomic diffusivity, in agreement with the interpretation described in Section II.

We also evaluated⁽³²⁾ the peak temperatures of the nucleation and growth reactions of the crystalline phase for the amorphous $Zr_{67}Cu_{33}$, $Zr_{65}Al_{7.5}Cu_{27.5}$ and $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloys by measuring the change in the peak temperature of the exothermic reaction due to crystallization as a function of annealing temperature (T_a) for the samples subjected to the preannealing treatment for 60 s at various T_a . Figure 7 plots the difference in the inverse of the peak temperature between the preannealed and the as-quenched samples ($1/T_p - 1/T_p^0$) as a function of annealing temperature (T_a). It is seen that the maximum phenomenon is observed for the $Zr_{65}Al_{7.5}Cu_{27.5}$ ternary and $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ quaternary alloys with larger glass-forming ability and no maximum phenomenon is

Fig. 6 Arrhenius plot of the incubation time (τ) for the precipitation of bct Zr_2Cu or $Zr_2(Cu, Al)$ phase for amorphous $Zr_{67}Cu_{33}$, $Zr_{65}Al_{7.5}Cu_{27.5}$ and $Zr_{65}Al_{20}Cu_{15}$ alloys.

Fig. 7 Relation of $(1/T_p - 1/T_p^0) \times 10^6/K$ and T_a for amorphous $Zr_{70}Cu_{30}$, $Zr_{65}Al_{7.5}Cu_{27.5}$ and $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloys.

seen for the $Zr_{70}Cu_{30}$ binary alloy. The maximum temperature has previously been reported⁽³³⁾ to correspond to the peak temperature of the nucleation reaction of the crystalline phase. The crystallization temperature (T_x) shown in Fig. 7 is measured at the fastest heating rate of 5.33 K/s in the DSC analysis and can be regarded as the peak temperature of the growth reaction of the crystalline phase. It is therefore said that the Zr–Al–Cu and Zr–Al–Ni–Cu alloys have the significant difference in the peak temperatures between the nucleation and growth reactions and the difference becomes more significant by the multiplication of the alloy components from the ternary to the quaternary system. It is generally known that the distinct difference in the peak temperatures of the nucleation and growth reactions causes the increase in the glass-forming ability through the increase in the thermal stability of the supercooled liquid, being consistent with the present result. By utilizing the difference in the peak temperatures of the nucleation and growth reaction, the tailor control of the particle size of the crystallization-induced phase has been reported⁽³⁰⁾ for the $Zr_{65}Al_{7.5}Cu_{27.5}$ alloy.

IV. Preparation and Properties of Bulk Amorphous Alloys in the New Ternary Systems

By choosing the above-described ternary alloys with the wide supercooled liquid region and the large glass-forming ability, we succeeded⁽³⁴⁾ in producing bulk amorphous alloys with a maximum thickness of about 10 mm in cylindrical and sheet shapes by the high-pressure die casting method, as exemplified for a $Mg_{80}Cu_{10}Y_{10}$ alloy in Fig. 8. It is seen that these cast samples have good metallic luster typical for amorphous alloys. The bulk

Fig. 8 Shape and surface appearance of an amorphous $Mg_{80}Cu_{10}Y_{10}$ alloy in cylindrical and sheet forms prepared by the high pressure die casting method.

$Mg_{80}Cu_{10}Y_{10}$ amorphous alloy exhibits high tensile strength exceeding 600 MPa at room temperature which is about three times as high as the highest strength⁽³⁵⁾ for conventional Mg-based cast alloys. The bulk amorphous alloys have large viscous flowability, as is evidenced from the high strain-rate sensitivity (m value) of 1.0⁽³⁶⁾ corresponding to the ideal Newtonian flow in the supercooled liquid region shown in Fig. 9. By utilizing the large viscous flow, the extremely large elongation above 15000% is obtained by tensile deformation of the bulk amorphous alloy in the supercooled liquid region⁽³⁷⁾, as shown in Fig. 10. We can also perform a blow deformation for the cast amorphous alloy sheet by applying one to two atmospheric pressures in the supercooled liquid region, resulting in the formation of an amorphous balloon with good surface luster shown in Fig. 11⁽³⁸⁾. Furthermore, the application of the die-forging treatment to the amorphous bulk in the supercooled liquid region causes the formation of a small amorphous gear with a smooth surface⁽³⁹⁾ which cannot be obtained for conventional superplastic crystalline alloys with the grain boundary sliding mechanism, as shown in Fig. 12.

Fig. 9 Relation between true stress (σ) and strain rate ($\dot{\epsilon}$) at 480 and 500 K in the supercooled liquid range for an amorphous $La_{35}Al_{25}Ni_{20}$ alloy.

Fig. 10 Shape and surface appearance of an amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy deformed up to 15000% by tensile load in the supercooled liquid region.

Fig. 11 Amorphous alloy balloon prepared by blow deformation through the application of one to two atmospheric pressures in the supercooled liquid region.

Fig. 12 Amorphous alloy gear prepared by die forging for 1000 s at 500 K under an applied load of 30 MPa.

V. Further Increase in Glass-Forming Ability by Multiplication of Components and Formation of Bulk Amorphous Alloys with Thicknesses Exceeding 10 mm

Figure 13 shows the relation between R_c and T_g/T_m for the new amorphous alloys in ternary and quaternary alloy systems, along with the data on the previously reported amorphous alloys and oxide glasses. It is to be noticed that the multiplication of alloy components from the ternary to quaternary systems causes a further decrease in R_c to 1 to 10 K/s which is almost comparable to that for oxide glasses. However, no appreciable change in T_g/T_m is seen between the ternary and the quaternary systems. On the other hand, the ΔT_x value increases significantly by the further multiplication and reaches 127 K for the $\text{Zr}_{65}\text{Al}_{17.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy⁽⁴⁰⁾, as shown in Fig. 14. The largest ΔT_x value is almost twice as large as the largest ΔT_x value⁽¹⁴⁾⁽¹⁵⁾ for Pd- and Pt-based amorphous alloys. The effect of the multiplication of alloy components with different atomic size ratios and large negative heats of mixing has later been confirmed through the evidence of the formation of amorphous alloys with ΔT_x of about 80 K in Zr-Ti-Ni-Cu-Be system⁽⁴¹⁾. It has subsequently been found⁽⁴²⁾⁽⁴³⁾ that the quaternary alloy can be amorphized into a bulk form with a maximum diameter of 16 mm and a length of 150 mm by quenching the molten alloy in a quartz tube into water. Figure 15 shows the outer surface appearance of the resulting bulk amorphous $\text{Zr}_{65}\text{Al}_{17.5}\text{Ni}_{10}\text{Cu}_{17.5}$ cylinder. The bulk alloy has a good white luster typical for metallic amorphous alloys. It has further been confirmed⁽⁴²⁾⁽⁴³⁾ that the bulk amorphous alloy with the diameter of 16 mm has the same T_g , ΔT_x , T_x

Fig. 13 Relation between R_c and T_g/T_m for the Zr-Al-TM (TM=Co, Ni, Cu) quaternary and pentenary alloys. The data of other metallic amorphous alloys and oxide glasses are also shown for comparison.

Fig. 14 Compositional dependence of ΔT_x for amorphous $\text{Zr}_{65}\text{Al}_{7.5}(\text{Co}, \text{Ni}, \text{Cu})_{27.5}$ alloys.

Fig. 15 Shape and surface appearance of a bulk amorphous $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy prepared by quenching the molten alloy in a quartz tube into water.

and ΔH_x values as those for the melt-spun ribbon sample with the thickness of $30\ \mu\text{m}$. Only the difference can be detected in the heat of structural relaxation of the amorphous samples and there is no appreciable difference in the specific heat of the supercooled liquid in an internal equilibrium state, as shown in Fig. 16.

From the cast bulk amorphous alloys, tensile testing specimens with gauge dimensions of 2 mm in diameter and 10 mm in length were prepared by mechanical cutting. The cast bulk amorphous $\text{Zr}_{60}\text{Al}_{10}\text{Co}_3\text{Ni}_9\text{Cu}_{18}$ alloy has a tensile fracture strength of about 1500 MPa and exhibits a serrated flow phenomenon just before final fracture⁽⁴⁴⁾⁽⁴⁵⁾. This serration is thought to result from the momentum stop of shear sliding deformation on the maximum shear plane because of the good ductility for the cast bulk alloy. The tensile fracture takes place on the maximum shear plane which is declined by about 45 degrees to the direction of tensile load and the fracture surface consists mainly of a well developed vein pattern as shown in Fig. 17. The diameter of the veins is about 10 times as large as that⁽³³⁾ for the melt-spun ribbon sample, indicating the remarkable extension of the deformation region resulting from the highly ductile nature of the cast bulk amorphous alloy.

Fig. 16 Temperature dependence of apparent specific heat $C_p(T)$ of the bulk amorphous Zr-Al-Ni-Cu cylinders with diameters of 10 and 16 mm. The data of the melt-spun ribbon are also shown for comparison. $C_{p,q}$ and $C_{p,s}$ represent the specific heat of the as-quenched sample and the sample heated once to 690 K, respectively.

VI. Preparation of Bulk Amorphous Alloys by Arc Melting

By choosing the quaternary or pentenary alloys in the Zr-Al-TM ($\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) system, we can produce bulk amorphous alloys by arc melting on a copper hearth⁽⁴⁶⁾. However, it is very difficult to suppress completely the precipitation of the Zr_2TM crystalline phase because of the ease of the heterogeneous nucleation at the bottom side contacted with a copper hearth, as exemplified in Fig. 18. Here, it is to be noticed that the amorphous phase is formed in the inner region where the heat flux reinforced from copper hearth disappears and the cooling capacity is reduced. That is, the low cooling rate obtained by arc melting is high enough to cause an amorphous phase in the Zr-Al-Co-Ni-Cu system. The crystalline phase can be divided into three different zones of outer equiaxed zone, columnar dendritic zone and metastable single phase zone, as illustrated in Fig. 19. It is further seen in Fig. 18 that the interface between the amorphous and crystalline phases is very smooth, because of the satisfaction of the highly supercooled solidification condition defined by the criterion of $V_i \gg D_i / \delta_i$ ⁽⁴⁷⁾. Here, V_i is the moving velocity of the liquid/solid interface, D_i is the diffusivity of the constituent elements at the interface and δ_i is the distance of the atomic rearrangement required for the formation of the solid phase from liquid. On the other hand, in the inner region which is far away from the copper hearth, one cannot take account of the effect of reinforced heat flux from the copper hearth. It is therefore expected⁽⁴⁸⁾ that the direction of heat flux agrees with that of grain growth and the interface becomes unstable and irregular. However, we can always observe a smooth interface even in the inner region, as shown in Fig. 20⁽⁴⁶⁾. Considering that the wave

Fig. 17 Tensile fracture surface appearance of a bulk amorphous $\text{Zr}_{60}\text{Al}_{10}\text{Co}_3\text{Ni}_9\text{Cu}_{18}$ alloy.

Fig. 18 Optical micrographs revealing the cross sectional structure of an amorphous $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ ingot prepared by arc melting.

Fig. 19 Schematic illustration showing the features and dominant parameters of the solidification structure of the arc-melted ingot.

length (λ_i) of the interface can be expressed by $\lambda_i = 2\pi(D\Gamma/V\Delta T_0)^{1/2}$, ($\Gamma = \sigma/\Delta S_f$, ΔT_0 is the temperature interval between liquidus and solidus temperatures)⁽⁴⁹⁾, the inconsistency is presumably because the present supercooled liquid has a large liquid/solid interface energy. This presumption is consistent with the interpretation (Section II) derived from the thermodynamical aspects. We have further confirmed⁽⁴⁶⁾ that the critical sample thickness (t_c) for formation of an amorphous phase in the Zr–Al–TM ingots prepared by arc melting tends to increase with increasing ΔT_x , even though the critical thickness includes the influence of the heterogeneous nucleation at the bottom side contacted with copper hearth. The strong correlation between t_c and ΔT_x indicates that

Fig. 20 Optical micrograph revealing the bct $Zr_2(Cu, Al, Ni)$ phase which precipitated in the inner region without reinforced heat flux from copper hearth.

Fig. 21 Shape and surface appearance of a bulk amorphous $Zr_{60}Al_{10}Ni_{10}Cu_{15}Pd_5$ alloy with a thickness of 10 mm, a width of 12 mm and a length of 300 mm prepared by a unidirectional zone melting method using an arc type heat source.

the large glass-forming ability for the present amorphous alloys is due to the high thermal stability of the supercooled liquid against the precipitation of the crystalline phase. The interpretation derived from the microscopic observation of amorphous and crystalline interface is consistent with that described in Sections II and III.

VII. Production of Continuous Bulk Amorphous Alloys by a Unidirectional Zone Melting Method

In any kinds of unidirectional zone melting methods, the cooling rate of the melt can be estimated from the product of the velocity of the liquid/solid interface (V) and the temperature gradient at the interface (G). With the aim of producing a continuous bulk amorphous alloy without limitation of sample length, we constructed a unidirectional zone melting equipment using an arc-type heat source⁽⁵⁰⁾ and the prealloyed $Zr_{60}Al_{10}Ni_{10}Cu_{15}Pd_5$ ingot was moved at a velocity of 5.7 mm/s. Since the width

of the alloy liquid on the copper hearth is 12 mm and the temperature of the alloy liquid is controlled to be about 2000 K, the resulting cooling rate is estimated to be of the order 2×10^3 K/s ($G \cdot V = dT/dz \cdot dz/dt = (2000/6) \cdot (5.7/1) \approx 2 \times 10^3$). The cooling rate has been confirmed⁽⁵¹⁾ to agree roughly with the cooling rate ($\approx 2.3 \times 10^3$ K/s) evaluated from the secondary dendrite arm spacing of Al-Cu binary alloy ingots with the same shape prepared by the same unidirectional solidification method. The cooling rate estimated thus exceeds largely the critical cooling rate for glass formation for the present Zr-Al-TM alloys. It is therefore expected that a continuous bulk amorphous alloy is produced by the present unidirectional zone melting method using an arc-type heat source. As an example, Fig. 21 shows the outer surface appearance of a zone-melted bulk amorphous $Zr_{60}Al_{10}Ni_{10}Cu_{15}Pd_5$ alloy with a thickness of 10 mm, a width of 12 mm and a length of about 300 mm⁽⁵⁰⁾. It is seen that the bulk alloy has a good white luster typical for a metallic amorphous phase. Figure 22 shows the DSC curves of the samples obtained from the sites which are away by 10 and 270 mm from the edge of the bulk alloy. Both the samples show the distinct glass transition, followed by the appearance of a wide supercooled liquid region and then large exothermic reaction due to crystallization and there is no appreciable difference in T_g , ΔT_x , T_x and ΔH_x , in spite of the significant difference of the sample sites. The appearance of the nearly constant properties indicates that the present unidirectional zone melting method is useful for the production of a continuous bulk amorphous alloy with a homogeneously mixed alloy composition, when an alloy with R_c much lower than about 10^3 K/s is used. The

Fig. 22 DSC curves of the samples taken from the sites which are away by about 10 and 270 mm from the edge of the bulk amorphous $Zr_{60}Al_{10}Ni_{10}Cu_{15}Pd_5$ alloy shown in Fig. 21.

success of producing the bulk amorphous alloy by this method also implies the significant relaxation of the shape and dimension of amorphous alloys which have been limited to thin sheet, fine wire and small powder shapes. It is therefore believed that the future progress of the science and engineering for amorphous alloys will be accelerated by utilizing the new amorphous alloys and the continuous preparation technique.

VIII. Conclusion

As described in the present review, the series of discoveries of new amorphous alloys having large glass-forming ability cause the drastic increase in the sample thickness to about 20 mm as well as the drastic change in the production method from melt spinning to conventional casting, arc melting and unidirectional zone melting, etc. These drastic changes allow us to expect the revisit to an amorphous age. Furthermore, considering that the discoveries of the new alloy compositions were made for the last five years, we can expect to have a similar drastic progress of alloy composition and production technique in the near future. The revisit of the amorphous alloy age is expected to raise drastically the value of the amorphous alloy as truly engineering materials.

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