Mg-Cu-Y Bulk Amorphous Alloys with High Tensile Strength Produced by a High-Pressure Die Casting Method

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Amorphous Mg-Cu-Y alloys with diameters (or thicknesses) ranging from 1 to 7 mm were formed in cylinder and sheet forms by using a high-pressure die casting process. The maximum diameter (or thickness) for formation of an amorphous phase was strongly dependent on composition and the largest value was obtained for Mg₆₅Cu₂₅Y₁₀. There is a tendency for the maximum diameter to increase with an increase in the supercooled liquid region. The glass transition temperature, crystallization temperature and heat of crystallization are independent of sample diameter in the range below 7 mm while the heat of relaxation decreases with increasing sample diameter, indicative of the formation of a more relaxed atomic configuration in the thicker samples. The tensile strength (σ_f) of the cast Mg₈₀Cu₁₀Y₁₀ alloy is 630 MPa at room temperature (RT), remains almost unchanged in the range below 353 K and then decreases to 395 MPa at 423 K, accompanying the significant increase in elongation. The σ_f at RT is about 80% as high as that for the corresponding melt-spun ribbon and the difference is presumably due to the existence of pores which are evaluated to be about 17%. It is thus concluded that the application of the high-pressure die casting technique to the alloys with large glass-forming ability is useful for the formation of the bulk amorphous alloys with high tensile strength.

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I. Introduction

It is known⁽¹⁾ that amorphization for most of metallic alloys by rapid solidification is usually achieved in the case of high cooling rates exceeding 10^4 K/s. The necessity of the high cooling rates causes the limitation to small values of sample thickness and diameter for the amorphous alloys. Accordingly, the formation of bulk amorphous alloys has been tried by various methods of warm extrusion⁽²⁾⁻⁽⁴⁾ and warm rolling⁽⁵⁾ of amorphous alloy powders at the temperatures below the crystallization temperature, shock consolidation⁽⁶⁾⁽⁷⁾, hydrostatic high-pressure sintering⁽⁸⁾, etc. However, the tensile strength of the bulk amorphous alloys produced by these consolidation methods is rather low and little have been reported about the data that the tensile strength is nearly the same as that for the melt-spun amorphous ribbon.

Recently, the present authors have found that new amorphous alloys with a wide supercooled liquid region in Mg-⁽⁹⁾⁽¹⁰⁾, La-⁽¹¹⁾⁽¹²⁾ and Zr-⁽¹³⁾⁽¹⁴⁾ based systems have large glass-forming ability and can be formed even by a metallic mold casting method⁽¹⁵⁾⁽¹⁶⁾. The cooling rate of the cylindrical samples achieved by the metallic mold casting method has been evaluated⁽¹⁶⁾ to be of the order 400 K/s for the diameter (d) of 1 mm and 120 K/s for

$d=3$ mm by the direct finite difference method⁽¹⁷⁾. The low critical cooling rates for formation of an amorphous phase for the Mg-, La- and Zr-based alloys allow us to expect that the application of a high-pressure die casting method causes the direct formation of bulk amorphous alloys with various net shapes. Furthermore, the development of the high-pressure die casting method as a new technique of producing an amorphous alloy seems to be important for further extension of practical fields in metallic amorphous alloys. This paper is intended to present the result that Mg-based bulk amorphous alloys with diameters ranging from 1 to 7 mm are formed by the high-pressure die casting method and exhibit high mechanical strengths and a wide supercooled liquid region. In addition, the cooling process is discussed on the basis of the data on the structural relaxation, glass transition and crystallization behavior for the Mg-based bulk amorphous alloys.

II. High-Pressure Die Casting Equipment

Figure 1 shows a schematic illustration of a newly designed high-pressure die casting equipment which consists mainly of sleeve and plunger for melting of mother alloy, a plunger to apply a high pressure through a hydraulic pressure, a casting copper mold with a high squeeze pressure and an evacuation system to eliminate gas in the crucible and mold immediately before casting. The sleeve and plunger were made from a heat-resistant tool steel (SKD61). The mother alloy is melted in the

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Fig. 1 Schematic illustration of a high-pressure die casting equipment used in the present study.

sleeve in an argon atmosphere with a high-frequency induction coil and cast into the copper mold by moving the plunger through a hydraulic pressure.

When the high-pressure die casting process is regarded as a kind of rapid solidification processes leading to the formation of an amorphous phase, the process is thought to have the following features:

- (1) The casting of a molten alloy into a mold is complete within several millisecond, leading to achievements of a significant quenching effect and a high production rate.
- (2) The application of high-pressure causes a good contact between molten alloy and mold, leading to the increase in cooling rate through the increase in heat flow and heat transfer coefficient at the die-melt interface as well as the formation of a net shape alloy.
- (3) Casting defects such as shrink holes which generate by the shrinkage during solidification are reduced.
- (4) Alloys with complicated shapes are produced directly from a liquidus state even for a molten alloy with high viscosity.

By taking advantage of these facts, it is expected that amorphous alloys with much larger shapes and dimensions than those obtained by the conventional melt spinning process can be formed in various alloy systems by the high pressure die casting process.

III. Experimental Procedure

Ternary Mg-Cu-Y alloys were used in the present study because their alloys had the widest supercooled liquid region in Mg-based alloy systems⁽¹⁶⁾. Their ingots

were prepared by induction-melting a mixture of pure Mg (99.99 mass%), Cu (99.99 mass%) and Y (99.99 mass%) metals in a purified argon atmosphere. The compositions are nominally expressed in atomic percent hereafter. From the master alloy ingots, cylindrical samples with lengths of 40 and 80 mm and different diameters of 1.0 to 9.0 mm and sheet samples with a length of 80 mm and different thicknesses of 0.5 to 9 mm were prepared by high-pressure die casting of the melt into copper molds with inner shapes of cylinder and sheet. The casting pressure, plunger velocity and holding time of applied pressure were 63 MPa, 1.7 m/s and 5 s, respectively, and the copper mold was cooled with flowing water. A die lubricant was not used in the present casting operation because the strip of the cast samples from the mold was easy. For comparison, an amorphous ribbon with a cross-section of about $0.02 \times 1 \text{ mm}^2$ was also produced by the single roller melt spinning method in an argon atmosphere.

The amorphicity of the as-cast samples in the cylinder and sheet forms was examined by X-ray diffractometry, transmission electron microscopy (TEM) and optical microscopy (OM) techniques. The specific heat (C_p) associated with structural relaxation, glass transition and crystallization was measured at a heating rate of 0.67 K/s with a differential scanning calorimeter (DSC). The heating rate was chosen because of the appropriateness for distinct detection of the glass transition phenomenon. The TEM samples were prepared by thinning electrolytically the cast sheet, which had previously thinned by mechanical polishing, in a solution of 20% nitric acid and 80% methanol at 273 K. Hardness was measured at room temperature by a Vickers microhardness tester with a 4.9 N load. The tensile strength of the as-cast sheet and melt-spun ribbon specimens and the compressive strength of the as-cast cylinder were measured in the temperature range of 293 to 473 K by an Instron-type tensile testing machine at a strain rate of $5.6 \times 10^{-4} \text{ s}^{-1}$ for the tensile strength and $4.2 \times 10^{-4} \text{ s}^{-1}$ for the compressive strength. The testing temperature was controlled by using a heating medium of silicon oil. Tensile and compressive specimens of the as-cast alloy were machined from the cast sheets into sheets having a gauge dimension of 3 mm in width and 0.5 mm in thickness and from the cast cylinders into cylinders having the dimensions of 2 mm diameter and 4 mm height, respectively. Also, the melt-spun ribbon was cut into strips having a gauge dimension of 20 mm long. Subsequent to tensile testings, the fracture surface appearance was examined by scanning electron microscopy (SEM). The melting temperature of the as-cast ingots was measured from the heating and cooling curves obtained at a scanning rate of 0.33 K/s with a differential thermal analyzer (DTA).

IV. Results and Discussion

1. Production of bulk amorphous alloys

Figure 2 shows the surface appearance of the as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ samples in the cylinder and sheet forms in which the diameter and thickness are in the range of 1 to 9 mm and 0.5 to 9 mm, respectively. The length of the sample is fixed to be 80 mm from the inner shape of the copper mold. As shown in the photograph, neither holes nor cavities are seen on the outer surface of the as-cast samples and their surface has a good luster. Considering that the shape and dimension of the as-cast samples shown in Fig. 2 are just the same as the inner shape of the copper mold, the high-pressure die casting method seems to be useful for the production of the Mg-Cu-Y bulk samples in net shape.

Figure 3 shows the X-ray diffraction patterns of the as-cast $\text{Mg}_{90-x}\text{Cu}_x\text{Y}_{10}$ ($x=10, 15, 20$ and 25 at%) cylinders with a fixed diameter of 3 mm. The cylinders have a broad diffraction peak around $K_p=25 \text{ nm}^{-1}$ and no diffraction peak corresponding to a crystalline phase is seen in all the samples, indicating that a mostly single amorphous phase is formed by the die casting method. The amorphicity of the as-cast samples was also confirmed by TEM. As an example, Fig. 4 shows the bright-field electron micrograph and selected area diffraction pattern taken from the central region in the as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinder with a diameter of 3 mm. No appreciable contrast revealing the existence of a crystalline phase is seen in the bright-field image and the diffraction pattern consists only of a broad halo ring. Figure 5 shows the X-ray diffraction patterns taken from the cross section in the as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinders with different diameters ranging from 1 to 9 mm, along with the result of a melt-spun Mg-Cu-Y ribbon with the same composition. The cylinders with diameters below 7 mm as well as the ribbon have only a broad diffraction peak at $K_p=25.34 \text{ nm}^{-1}$, though some diffraction peaks corresponding to a crystalline phase are seen in the cylinder

sample with a diameter of 9 mm. This result indicates that the critical diameter for formation of an amorphous single phase is in the range between 7 and 9 mm. Furthermore, no appreciable difference in the K_p value is observed among the three samples in cylinder and ribbon forms. The agreement indicates that there is no significant change in the amorphicity of the Mg-Cu-Y samples prepared by casting and melt spinning, in spite of the large difference in cooling rate of the melt. In addition, it is said that the $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ alloy has the large glass-forming ability enough to produce an amorphous single phase even with a large diameter of 7 mm.

It is generally known that die-cast alloys include a rather large volume fraction of pores resulting from the

Fig. 3 X-ray diffraction patterns taken from the cross section in $\text{Mg}_{90-x}\text{Cu}_x\text{Y}_{10}$ ($x=10, 15, 20$ and 25 at%) cylinders with a diameter of 3 mm produced by high-pressure die casting.

Fig. 2 Surface appearance of $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ samples in cylindrical and sheet forms produced by high-pressure die casting.

Fig. 4 Bright-field electron micrograph and selected area diffraction pattern taken from the central region of an amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinder with a diameter of 3 mm.

Fig. 5 X-ray diffraction patterns taken from the cross section in as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinders with diameters of 1 to 9 mm.

involvement of gas. The size and distribution of the pores were examined for the present die-cast alloys. Figure 6 shows an optical micrograph revealing a transverse cross-sectional surface in an unetched state for the as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinder with a diameter of 3 mm. Although no contrast corresponding to the precipitation of any crystalline phases is seen over the entire transverse cross section, a number of dark spots with sizes of 5 to 40 μm are distributed homogeneously. The dark spots have previously been confirmed to correspond to pores by SEM and hence the porosity for the present Mg–Cu–Y cylinders produced by the high-pressure die casting method is evaluated to be about 17%. In addition, as shown in Fig. 6, the distribution of the pores is very uniform and no distinct change in the porosity is seen between the central region and the surface region. The uniform distribution of the small pores indicates that the cylinder was cast at a rather high cooling rate so as to suppress both the coalescence of pores and the annihilation of pores from the surface. The porosity is about 15% for $d=1$ mm, 17% for $d=3$ mm and 16% for $d=7$ mm, being independent of the sample diameter, i.e., the cooling rate of the samples.

From the X-ray diffraction patterns (Fig. 5) taken from the transverse cross section, it is concluded that the cylinder with a diameter of 9 mm consists of the amorphous and crystalline phases. However, the X-ray diffraction pattern taken from the surface of the cylindrical sample consists only of a broad halo peak as shown in Fig. 7, indicating that the surface region of the cylindrical sample is composed of an amorphous phase even with a large

Fig. 6 Optical micrograph revealing the cross sectional surface of an amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinder with a diameter of 3 mm.

Fig. 7 X-ray diffraction pattern taken from the outer surface in an as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinder with a diameter of 9 mm.

diameter of 9 mm. Figure 8 shows the transverse cross section of the $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinder with a diameter of 9 mm. It is seen that the contrast is distinctly different between the central region and the surface region and the surface region with a thickness of 2 mm has a much better luster. Judging from the result that the luster is much better for the amorphous phase than for the crystalline phase, it is said that the amorphous phase is formed within the thickness of about 2 mm from the surface. Accordingly, it appears important to point out that the

Fig. 8 Optical micrograph revealing the transverse cross section of an as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinder with a diameter of 9 mm.

Fig. 9 Maximum diameters for formation of an amorphous single phase for as-cast $\text{Mg}_{90-x}\text{Cu}_x\text{Y}_{10}$ cylinders.

high-pressure die casting technique is also useful for the production of the structurally gradient materials in which the surface region is composed of an amorphous phase. Figure 9 shows the compositional dependence of

the critical diameter for formation of an amorphous phase in the $\text{Mg}_{90-x}\text{Cu}_x\text{Y}_{10}$ cylinders produced by the high-pressure die casting method. The critical diameter (d_c) is 3 mm for $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ and increases significantly with increasing Cu content. The largest d_c value of 7 mm is obtained for $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ and further increase in Cu content causes a decrease in d_c . As shown later, the significant compositional dependence in d_c reflects the stability of the supercooled liquid which is observed in the temperature range below T_x .

2. Thermal stability

The DSC curves of the amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinders with different diameters are shown in Fig. 10, along with that of the melt-spun amorphous ribbon. Here, T_g marked with arrows represents the temperature at which the curvature of specific heat curve as a function of temperature, $C_p(T)$, (see Fig. 13) is the largest in the glass transition temperature range. T_g and T_x of the bulk samples are 420 and 490 K, respectively, independent of the diameter of the cylinders. Furthermore, there is no appreciable difference in the T_g and T_x values between the cast and melt-spun samples. The heat of crystallization (ΔH_x) was measured to be 3.63 to 3.47 kJ/mol for the cylinders with diameters of 1 to 7 mm and 3.57 kJ/mol for the ribbon, being nearly the same in the five samples. It is thus concluded that the sequent transition behavior of glass transition, supercooled liquid and crystallization is independent of the preparation conditions. In addition, Fig. 11 shows the compositional dependence of the DSC curve for the $\text{Mg}_{90-x}\text{Cu}_x\text{Y}_{10}$ cylinders with a diameter of 3 mm. The change in the DSC curves with Cu content for the cylinders is just the same as that⁽¹⁷⁾ for the melt-spun ribbons. The temperature interval between T_g and T_x , $\Delta T_x (= T_x - T_g)$, on the DSC curves shown in Figs. 10 and 11 corresponds to the supercooled liquid

Fig. 10 DSC curves of amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinders with diameters of 1 to 7 mm.

Fig. 11 DSC curves of amorphous $\text{Mg}_{90-x}\text{Cu}_x\text{Y}_{10}$ cylinders with a diameter of 3 mm.

region and there is a clear tendency for ΔT_x to increase with increasing Cu content from 10 to 25%. ΔT_x has a strong correlation with d_c and it is seen in Fig. 12 that d_c increases with increasing ΔT_x . Considering the previous result⁽¹⁵⁾ that ΔT_x is roughly proportional to the glass-forming ability, it is concluded that the change in d_c is due to that in the glass-forming ability.

It is reasonable to consider that the cooling rate of the Mg-Cu-Y alloys is significantly different between the cylinder samples and the melt-spun ribbon and hence these samples have a significantly different disordered state. The difference in the disordered state was examined by measuring the enthalpy released during continuous heating. Figure 13 shows the thermograms of the amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinders with different diameters of 2 to 5 mm produced by casting, along with those of the melt-spun amorphous ribbon. Similar thermograms are seen in the three samples. As the temperature rises, the C_p value of the amorphous bulks increases gradually and begins to decrease, indicating an irreversible structural relaxation at 355 K (T_r) for the 2 mm cylinder and 365 K for the 5 mm cylinder. With a further increase in temperature, the C_p value shows its minimum in the temperature range of 395 to 400 K, then increases rapidly in the glass transition range from 405 to 440 K and reaches 42 J/mol·K for the supercooled liquid around 440 K. The C_p value of the supercooled liquid decreases slightly to 41

Fig. 12 Correlation between the critical diameter for formation of an amorphous phase and the temperature interval between T_g and T_x , $\Delta T_x (=T_x - T_g)$ for amorphous Mg-Cu-Y cylinders produced by high-pressure die casting.

Fig. 13 The thermogram of amorphous $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ cylinders with different diameters. The data of the corresponding melt-spun ribbon are also shown for comparison.

$\text{J/mol} \cdot \text{K}$ with increasing temperature in the range of 440 to 470 K. Above 470 K, the supercooled liquid crystallizes at 480 K, accompanied by ΔH_x of 3.5 kJ/mol as described in Fig. 10. It is also seen in Fig. 13 that the cast samples have a large difference, $\Delta C_{p,s \rightarrow l}$ in specific heat between the reheated amorphous solid and supercooled liquid reaching 19.5 J/mol·K. The difference in $C_p(T)$ between the as-cast and the reheated states, $[\Delta C_p(T)]$, manifests the irreversible structural relaxation which is presumed to arise from the annihilation of quenched-in “defects” and the enhancement of the topological and chemical short-range ordering through the atomic arrangement. The heat of the irreversible structural relaxation, ΔH_r ($\equiv \int \Delta C_p dT$, $\Delta C_p = C_{p,s} - C_{p,q} \geq 0$), was evaluated to be 385 J/mol for the 2 mm cylinder and 330 J/mol for the 5 mm cylinder. Comparing the thermograms of the cast samples with that of the melt-spun ribbon, it should be noticed that the former samples have higher values by 10 to 20 K for T_r and smaller values by 175 to 230 J/mol for ΔH_r and there are no significant differences in T_g , $\Delta C_{p,s \rightarrow l}$, T_x and ΔH_x . The smaller ΔH_r values for the cast samples imply that the amorphous phase produced by die casting has a more relaxed atomic configuration as compared with that for the melt-spun amorphous phase because of the lower cooling rate. Furthermore, it is seen in Fig. 13 that the 2 mm cylinder has a lower T_r and a larger ΔH_r as compared with those for the 5 mm cylinder, even though no appreciable difference is seen in the T_g and ΔH_x .

3. Mechanical properties

Figure 14 shows the nominal tensile stress and elongation curves of the $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ amorphous sheet tested at

Fig. 14 The temperature dependence of nominal tensile stress-elongation curve of amorphous $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ sheets with a thickness of 0.5 mm and a width of 3 mm.

different temperatures between 293 and 473 K. The feature of the stress-elongation curves can be divided into the following three types. That is, (1) high fracture stress and no appreciable elongation at 293 K, (2) high yield stress and small elongation in the temperature range of 353 to 393 K, (3) a clear yield phenomenon, followed by a significant decrease in nominal flow stress, accompanying large elongation in the range above 423 K. On the basis of the nominal stress-elongation curves shown in Fig. 14, the fracture stress at 293 K, the proof stress at a fixed elongation of 0.2% and elongation are plotted as a function of temperature in Fig. 15. The fracture stress is 630 MPa at 293 K, remains almost unchanged at the temperatures up to 353 K and then decreases rapidly with increasing temperature. Thus, the high proof stress exceeding 400 MPa is kept in the temperature range below 373 K. On the other hand, the elongation is below 7% in the temperature range below 393 K, because of inhomogeneous deformation and fracture behavior without distinct work-hardening, and increases rapidly to about 37% in the temperature range above 400 K, because of the significant viscous flow. In comparison with the previous data⁽¹⁶⁾ on the compressive proof stress of $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ cylinders⁽¹⁶⁾ produced by the metallic mold casting process and the tensile strength of a melt-spun $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ ribbon⁽¹⁸⁾, the tensile fracture strength at room temperature and the proof stress at 373 K for the present bulk sample are about 77 and 80%, respectively. It has been shown⁽¹⁶⁾ that the cylinder samples with a

Fig. 15 Changes in $\sigma_{0.2}$, σ_t and ϵ_t of amorphous $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ sheets with testing temperature.

diameter of 1.5 mm produced by the metallic mold casting process do not include distinct pores and the porosity is nearly equal to zero. On the contrary, the porosity in the present cylindrical samples is evaluated to be 17% as shown in Fig. 6. By taking the porosity into consideration, the decrease in the fracture strength and proof stress for the present cylinder samples is presumably due to the decrease in the true cross-sectional area resulting from the existence of the pores. Furthermore, from the approximate agreement among the compressive strength for the cylindrical sample without pores, the tensile strength of the melt-spun ribbon and the true tensile strength for the cylindrical sample with

17% porosity, it is concluded that the strength for the present Mg-Cu-Y amorphous cylinders is insensitive to stress concentration resulting from the existence of pores. The insensitivity is presumably due to the high toughness and large ductility for the amorphous Mg-Cu-Y cylinders produced by the high-pressure die casting method.

In order to investigate the reason for the distinction of the deformation behavior into the three types, the temperature dependence of the tensile fracture surface appearance of the sheet samples was examined by SEM. The micrographs shown in Fig. 16(a), (b) and (c) reveal the tensile fracture surface appearance of the $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ amorphous sheet fractured at 293 K, 373 K and 423 K, respectively. Although no appreciable necking is seen in the sample fractured at 293 K, the necking begins to occur at 373 K and is significant at 423 K. Furthermore, the vein pattern caused by the final adiabatic fracture which is observed on the fracture surface also appears to become distinct with increasing testing temperature. These changes indicate that the viscous flow begins to occur at 373 K and becomes remarkable with increasing test temperature, in agreement with the interpretation derived from the stress-elongation curves.

V. Summary

By using the high-pressure die casting technique, the production of bulk amorphous alloys in cylinder and sheet forms was tried for Mg-Cu-Y alloys with large glass-forming ability. Furthermore, the thermal stability and mechanical properties of the Mg-based bulk amorphous alloys were examined in comparison with those for the corresponding melt-spun ribbons. The results obtained are summarized as follows.

(1) Bulk amorphous alloys with diameters (or thicknesses) in the range of 1 to 7 mm were formed by the die casting process and the critical diameter (or thickness),

Fig. 16 Scanning electron micrographs revealing the tensile fracture surface appearance of amorphous $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ sheets fractured at 293 K, 373 K and 423 K.

d_c , is strongly dependent on alloy composition. The largest diameter was obtained for $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ with the widest supercooled liquid region before crystallization. Thus, there is a clear tendency for d_c to increase with increasing ΔT_x .

(2) T_g , T_x and ΔH_x of the bulk $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ amorphous alloy are independent of sample thickness and are nearly the same as those for the corresponding melt-spun ribbon with a thickness of about 0.02 mm. On the other hand, the onset temperature for structural relaxation (T_r) and the heat for relaxation (ΔH_r) are strongly dependent on the sample thickness. The increase in the sample thickness causes an increase in T_r and a decrease in ΔH_r , indicating that the thicker sample has a more relaxed amorphous structure.

(3) The ultimate tensile strength (σ_f) of the bulk $\text{Mg}_{80}\text{Cu}_{10}\text{Y}_{10}$ alloy is 630 MPa at room temperature, remains almost unchanged in the range below 353 K and decreases significantly to 395 MPa at 423 K, accompanying a significant increase in elongation. The σ_f value at room temperature is about 80% as high as that for the melt-spun ribbon. The decrease in σ_f by about 20% is presumably because of the existence of 20% in porosity.

From the achievement of the true tensile strength which is nearly the same as that for the melt-spun ribbon, it is concluded that the high-pressure die casting process is useful for the production of bulk amorphous alloys with high mechanical strengths for the alloy systems

having a large glass-forming ability.

REFERENCES

- (1) H. S. Chen: Rep. Prog. Phys., **43** (1980), 353.
- (2) H. H. Liebermann: Mater. Sci. Eng., **46** (1980), 241.
- (3) J. F. Lakner: Physica, **139 & 140B** (1986), 816.
- (4) Y. Kawamura, M. Takagi, M. Akai and T. Imura: Mater. Sci. Eng., **98** (1988), 449.
- (5) P. H. Shingu: Mater. Sci. Eng., **97** (1988), 137.
- (6) C. F. Cline and R. W. Hopper: Scripta Met., **11** (1977), 1137.
- (7) D. G. Morris: Metal Science, no. 6, (1980), p. 215.
- (8) Y. Kawamura, M. Takagi, M. Senoo and T. Imura: Mater. Sci. Eng., **98** (1988), 415.
- (9) A. Inoue, K. Ohtera, K. Kita and T. Masumoto: Jpn. J. Appl. Phys., **27** (1988), L2248.
- (10) A. Inoue, M. Kohinata, K. Ohtera, A. P. Tsai and T. Masumoto: Mater. Trans., JIM, **30** (1989), 378.
- (11) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans., JIM, **30** (1989), 965.
- (12) A. Inoue, H. Yamaguchi, T. Zhang and T. Masumoto: Mater. Trans., JIM, **31** (1990), 104.
- (13) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans., JIM, **31** (1990), 177.
- (14) T. Zhang, A. Inoue and T. Masumoto: Mater. Trans., JIM, **33** (1992), in press.
- (15) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans., JIM, **31** (1990), 425.
- (16) A. Inoue, A. Kato, T. Zhang, S. G. Kim and T. Masumoto: Mater. Trans., JIM, **32** (1991), 609.
- (17) I. Ohnaka and T. Fukusako: Trans. ISIJ, **21** (1981), 485.
- (18) S. G. Kim, A. Inoue and T. Masumoto: Mater. Trans., JIM, **31** (1990), 929.