Bulky La–Al–TM (TM = Transition Metal) Amorphous Alloys with High Tensile Strength Produced by a High-Pressure Die Casting Method

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The application of a high-pressure die casting technique to La–Al–TM (TM = Co, Ni, Cu) alloys was found to produce bulk amorphous alloys in cylinder and sheet forms. The maximum sample diameter (d) for formation of an amorphous phase is 3 mm for La₉₈Al₂Ni₁Cu₂₀, 7 mm for La₉₈Al₁₉Ni₆Cu₁₀ and above 9 mm for La₉₆Al₂Cu₁₉Ni₁₅Co₁₇. There is a clear tendency for d to increase with an increase in the temperature interval of a supercooled liquid region. The glass transition temperature (Tg), the crystallization temperature (Tc) and the heat of crystallization (ΔHc) remain unchanged in the thickness range of 1 to 7 mm for the La₉₈Al₁₉Cu₁₀Ni₁₀ alloy. Tg and ΔHc are nearly the same as those for the melt-spun ribbon. The tensile fracture strength (σf) and elongation (εf) for the La₉₈Al₁₉Cu₁₉Ni₁₅Co₁₇ cylinder with a diameter of 3 mm are 700 MPa and 1.5%. Although the εf value is nearly the same as that for the melt-spun ribbon, the σf value is about 80% as high as that for the ribbon. The decrease in σf by 20% is presumably due to the existence of pores based on the result that the porosity of the cast samples is about 20%. The achievement of the σf for the cast alloys with 20% in porosity indicates that the bulk amorphous alloys also have a ductile nature which is comparable to that for the melt-spun ribbon.

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I. Introduction

Recently, new amorphous alloys with a large glass-forming ability have been found in Mg-, La- and Zr-based alloys such as the Mg–Ln–TM⁰, La–Al–TM⁰ and Zr–Al–TM⁰ (Ln = lanthanide metal, TM = transition metal) systems. It has further been reported that these amorphous alloys are formed in a bulk form by a metallic mold casting method⁹ as well as by a water quenching method⁹. The maximum diameter of the bulk amorphous cylinders is in the range of 1 to 4 mm, depending on the alloy composition. Judging from the result⁹ that the cooling rate of the Mg-based alloys in the metallic mold casting process calculated by the use of the direct finite difference method⁸ is about 390 K/s for d = 1 mm and 92 K/s for d = 4 mm, the critical cooling rate for formation of their amorphous alloys is as small as 100 to 400 K/s. It is expected that a high-pressure die casting process has a much higher cooling rate as compared with that for the conventional metallic mold casting process. It is of importance to examine the critical sample thickness for formation of an amorphous single phase for the Mg-, La- and Zr-based alloys with large glass-forming ability by the use of the high-pressure die casting process. Little has been reported about the production of bulk amorphous alloys by the high-pressure die casting process and their thermal stability and mechanical properties. This paper is intended to present the critical sample thickness for formation of an amorphous phase in La–Al–TM (TM = Co, Ni, Cu) alloys by the high-pressure die casting method and the thermal stability and tensile strength of the resulting 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 sleeve and mold immediately before casting. The mother alloy is melted in the 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. 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.

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 com-
plete within several milisecond, leading to achievements of significant quenching effect and high production rate.

(2) The application of high-pressure causes a good contact between molten alloy and mold, leading to the formation of a net shape alloy, as well as the increase in cooling rate through the increase in heat flow and heat transfer coefficient at the die-melt interface.

(3) Defects inherent to casting such as shrinkage holes which generate by shrinkage during solidification are reduced.

(4) Alloys with net shapes are produced directly from a liquidus state even for a molten alloy with high viscosity.

By taking these advantages, it is expected that an amorphous alloy with shape and dimension which cannot be obtained by the conventional melt-spinning process is obtained in various alloy systems.

III. Experimental Procedure

Ternary, quaternary and penternary alloys in the La–Al–TM (TM=Co, Ni, Cu) systems were used in the present study because their alloys had a supercooled liquid region which was wider than that for Pd–Ni–Si, Pd–Cu–Si and Pt–Ni–Si amorphous alloys. Their ingots were prepared by arc melting a mixture of pure La (99.9 mass%), Al (99.99 mass%) and TM (above 99.9 mass%) metals in a purified argon atmosphere. The compositions are nominally expressed in atomic per cent hereafter. From the master alloy ingots, cylindrical samples with lengths of 40 and 80 mm and diameters ranging from 1 to 9 mm and sheet samples with a length of 40 mm and thicknesses ranging from 1 to 9 mm were prepared by high-pressure die casting of the melt into copper molds with inner shapes of cylinder and sheet. For comparison, an amorphous ribbon with a cross section of about 0.02 × 1 mm² was also produced by the 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 and optical microscopy 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 differential scanning calorimetry (DSC). Hardness was measured at room temperature by a Vickers microhardness tester with a 4.9 N (500 gf) load. Tensile strength of the as-cast cylinder was measured at room temperature by an Instron-type tensile testing machine at a strain rate of 8.33 × 10⁻⁴ s⁻¹. Tensile specimens of the as-cast alloys were machined from the cast cylinders into cylinders having a gauge dimension of 10 mm × 2 mm. Subsequent to tensile tests, the fracture surface appearance was examined by scanning electron microscopy (SEM). The melting temperature of the as-cast ingots was measured at a scanning rate of 0.33 K/s with a differential thermal analyzer (DTA).

IV. Results

Figure 2 shows the surface appearance and cross sectional shape of the as-cast La₅₃Al₁₂Ni₁₀Cu₁₀ samples in the cylinder and sheet forms in which the diameter and thickness are in the range of 1 to 9 mm and 3 to 9 mm, respectively. The length of the sample is fixed to be 40 and 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. 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 and hence the high-pressure die casting method is concluded to be useful for the production of the bulk La_{55}Al_{25}Ni_{10}Cu_{10} samples with various shapes and dimensions.

Figure 3 shows the X-ray diffraction patterns of the as-cast La_{55}Al_{25}Ni_{10}Cu_{10} cylinders with diameters of 5, 7 and 9 mm. The cylinders have a broad diffraction peak at $K_{\alpha} = 22.1$ nm$^{-1}$ and no diffraction peak corresponding to a crystalline phase is seen for all the samples, indicating that a mostly single amorphous phase forms even at a diameter of 9 mm by the die casting method.

The DSC curves of the amorphous La_{55}Al_{25}Ni_{10}Cu_{10} cylinders are shown in Fig. 4. $T_g$, $T_x$, and $T_{x-h}$ of the bulk samples are 460 and 527 K, respectively, independent of the diameter of the cylinders. On the basis of the DSC curves shown in Fig. 4, $T_g$, $T_x$, and the heat of crystallization ($\Delta H_x$) for the La_{55}Al_{25}Ni_{10}Cu_{10} cylinders are plotted as a function of sample diameter in Fig. 5. $T_g$ and $T_x$ are independent of diameter in the entire diameter range of 1 to 9 mm, but $\Delta H_x$ remains almost constant in the diameter range of 1 to 7 mm and then decrease by about 15%, respectively, for the diameter of 9 mm. Furthermore, since $T_g$, $T_x$, and $\Delta H_x$ for the melt-spun ribbon with a thickness of about 0.02 mm have been measured to be 460 K, 550 K and 4.90 kJ/mol, respectively, no appreciable difference is seen for $T_g$ while $T_x$ and $\Delta H_x$ decrease by about 4.2 and 4.1%, respectively, for the cylinder samples with diameters below 7 mm. In addition, we also confirmed that the $T_g$, $T_x$, and $\Delta H_x$ values of the cylinder samples with diameters below 7 mm agree with those of the melt-spun ribbon which was prepared by using the as-cast cylinder as a mother alloy. From these data on the thermal stability, it is concluded that the cylinder samples in the diameter range below 7 mm have a mostly single amorphous phase and the further increase in diameter causes the precipitation of a crystalline phase of about 15% into the amorphous matrix. The differences in $T_x$ and $\Delta H_x$ between the present cylinders and the previous melt-spun ribbons are presumably due to the deviation of alloy composition resulting from the difficulty of the complete protection of the molten alloy in the crucible crucible against oxidation.

As shown in Fig. 5, the La_{55}Al_{25}Ni_{10}Cu_{10} cylinder with a diameter of 9 mm seems to contain a crystalline phase of about 15% and the change into the coexistent structure is thought to originate from the lack of glass-forming ability. The partial replacement of 10% Ni in the La_{55}Al_{25}Ni_{10}Cu_{10} alloy by 5 at% Co has been reported to cause an increase in the temperature interval between $T_g$ and $T_x$, $\Delta T_x (= T_x - T_g)$. From the previous relation that the glass-forming ability increases with an increase of $\Delta T_x$, the glass-forming ability seems to be larger for the La_{55}Al_{25}Cu_{10}Ni_{5}Co_{5} alloy than for the La_{55}Al_{25}Cu_{10}Ni_{10} alloy. Figure 6 plots $T_g$, $T_x$ and $\Delta T_x$.
ΔH, as a function of sample thickness for the La_{55}Al_{25}Ni_{10}Co_{10} sheet samples produced by high-pressure die casting. All the properties of T_g, T_m and ΔH, remain constant in the entire thickness range, indicating the formation of a mostly single amorphous phase even at a large thickness of 9 mm. As in the case with the La_{55}Al_{25}Cu_{10}Ni_{10} alloy, the slight decrease in T_g for the La_{55}Al_{25}Cu_{10}Ni_{10}Co_{10} sheet samples is also presumed to result from the deviation of alloy component.

The cross-sectional structure for the La_{55}Al_{25}Cu_{10}Ni_{10}Co_{10} cylinder with a diameter of 9 mm was examined by optical and scanning electron microscopy with the aim of confirming the amorphism over the whole cross section and determining the porosity due to the involvement of gas. Figure 7(a) and (b) show the optical micrographs of the surface and central regions, respectively, for the cylinder with a diameter of 9 mm. No contrast revealing the existence of a crystalline phase is seen even in the central region with the smallest cooling rate. However, one can see uniformly distributed dark spots with sizes ranging from 2 to 25 μm. We confirm by SEM that the dark spots correspond to pores and hence the porosity of the cylindrical sample with a diameter of 9 mm is measured to be about 20%.

Table 1 summarizes the maximum diameter (d_m) for the formation of an amorphous single phase in the La-Al-TM alloys, along with the previous data of ΔT_s and T_g/T_m which have been considered to have a strong correlation with the glass-forming ability. The multiplication of the alloy components from the ternary to quaternary system through the quaternary system causes a distinct increase in maximum diameter, accompanying a significant increase in ΔT_s. However, the T_g/T_m has a high value of ≈0.60 for all the alloys and no distinct correlation is seen between T_g/T_m and the maximum diameter. This result indicates that the formation of these amorphous bulks with large diameters is due to the large glass-forming ability resulting from the increase in ΔT_s. It has previously been pointed out that the increase in ΔT_s originates from the difficulty in the nucleation and growth of a crystalline phase even in a supercooled liquid where the constituent elements have a rather large atomic diffusivity.

Here, it appears important to describe the effect of the ratio of surface area of the cast sample (A) to its volume (V) on the critical sample thickness for formation of an amorphous phase. It is well known that the cooling rate of a cast alloy is proportional to A/V. The above-described data in this paper were obtained from the cylinder with a circular cross section and hence A/V is larger for the cylinder in comparison with that for the sheet sample with a rectangular cross section in which the width is 10 mm and the thickness is equal to the diameter of the cylinder. If the sheet sample with a smaller A/V ratio is produced by the high-pressure die casting method, the critical sample thickness for formation of an amorphous phase is expected to decrease because of the decrease in cooling rate. For instance, the critical thicknesses for the La_{55}Al_{25}Ni_{20} and La_{55}Al_{25}Cu_{20} alloys...
Table 1  Maximum diameter for formation of an amorphous single phase ($d_c$) in the La–Al–TM system by high-pressure die casting. The data of $\Delta T_c$ and $T_e/T_m$ were taken from Refs. (3) (4) (12).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$d_c$ (mm)</th>
<th>$\Delta T_c$ (K)</th>
<th>$T_e/T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La_{51}Al_{12}Ni_{38}$</td>
<td>3</td>
<td>69</td>
<td>0.71</td>
</tr>
<tr>
<td>$La_{51}Al_{12}Cu_{38}$</td>
<td>3</td>
<td>58</td>
<td>0.68</td>
</tr>
<tr>
<td>$La_{51}Al_{12}Ni_{38}Cu_{10}$</td>
<td>5</td>
<td>88</td>
<td>0.70</td>
</tr>
<tr>
<td>$La_{51}Al_{12}Cu_{38}Ni_{10}Co_5$</td>
<td>$&gt; 9$</td>
<td>98</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Fig. 7  Optical micrographs revealing the microstructure in the surface (a) and central (b) regions of an amorphous $La_{51}Al_{12}Cu_{38}Ni_{10}Co_5$ cylinder with a diameter of 9 mm.

were determined to be 2 mm for the sheet samples, being smaller than 3 mm for the cylinder samples. Considering that the other casting conditions remain unchanged in the production of the sheet and cylinder samples, the decrease in the critical thickness seems to be attributed to the decrease in cooling rate of the cast alloy through the decrease in $A/V$. This presumption is also supported from the approximate agreement between the ratio (0.67)
of the critical sheet thickness to the critical cylinder diameter and the ratio (0.65) of the A/V value for the sheet with a thickness of 3 mm to that for the cylinder with a diameter of 3 mm.

It is thought that the cooling rate of the La-based alloys is significantly different between the cylinder samples and the melt-spun ribbon and hence these samples have significantly different disordered states. The difference in the disordered state was examined by measuring the enthalpy released during continuous heating. Figure 8 shows the thermograms of the amorphous La_{50}Al_{30}Ni_{10}Cu_{10} cylinders with different diameters of 1 to 7 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 apparent specific heat \(C_p\) of the amorphous bulk increases gradually and then decreases, indicating an irreversible structural relaxation at 382 K \((T_s)\) for the 1 mm cylinder, 389 K for the 3 mm cylinder and 399 K for the 7 mm cylinder. With a further increase in temperature, the \(C_p\) value shows its minimum in the temperature range of 440 to 450 K, then increases rapidly in the glass transition range from 460 to 500 K and reaches 42.0 J/mol·K for the supercooled liquid around 500 K. The \(C_p\) value of the supercooled liquid remains almost constant in the higher temperature range of 500 to 530 K. Above 530 K, the supercooled liquid crystallizes at 537 K, accompanied by \(\Delta H_s\) of 4.7 kJ/mol as described in Fig. 5. It is also seen in Fig. 8 that the cast samples have a large difference, \(\Delta C_p,T=1\) in specific heat between the reheated amorphous solid and supercooled liquid reaching 12.4 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 rearrangement. The heat of the irreversible structural relaxation, \(\Delta H_s(=\int \Delta C_p dT, \Delta C_p=C_p,T-C_p,\infty)=0\), was evaluated to be 575 J/mol for the 1 mm cylinder, 500 J/mol for the 3 mm cylinder and 380 J/mol for the 7 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 11 to 28 K for \(T_s\) and smaller values by 305 to 500 J/mol for \(\Delta H_s\) and there are no significant differences in \(T_s, \Delta C_p,T=1, T_s,\) and \(\Delta H_s\). The smaller \(\Delta H_s\) 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. 8 that the 1 mm cylinder has a lower \(T_s\) and a larger \(\Delta H_s\) as compared with those for the cylinders with diameters of 3 to 7 mm, even though there is no appreciable difference in \(T_s\) and \(\Delta H_s\).

In order to evaluate the significance of the high-pressure die casting technique, it is of importance to clarify whether or not the La-Al-Cu-Ni-Co amorphous cylinders exhibit a high tensile strength which is nearly the same as that for the corresponding melt-spun ribbon. Figure 9 shows the nominal tensile stress-elongation curve at room temperature for the La_{50}Al_{30}Cu_{10}Ni_{10}Co_{10} cylinder with a diameter of 3 mm, along with the shape and dimensions of the sample used for the tensile test. The tensile strength and the fracture elongation including elastic elongation are 700 MPa and 1.5%, respectively, which are about 80% as high as those (880 MPa and 2.0%) for the melt-spun La-Al-
Cu-Ni-Co ribbon sample with a thickness of about 20 μm. The tensile fracture surface appearance of the cylinder sample is shown in Fig. 10. Vein pattern typical for an amorphous alloy with good bending ductility is observed over the whole fracture surface. However, as marked with arrows in Fig. 10(b), some pores with sizes of 2 to 25 μm are seen in the fracture surface and the area fraction occupied by the pores is measured to be about 20% which is nearly the same as the porosity (±20%) evaluated from the optical micrographs of the cross section shown in Fig. 7. Here, it appears important to point out that the true fracture strength evaluated by taking the porosity into the consideration is 875 MPa which is nearly the same as that (880 MPa) for the melt-spun ribbon. The approximate agreement suggests that the La-Al-Cu-Ni-Co amorphous cylinder has a good ductility and the existence of pores does not exert harmful influence on the tensile strength. It is therefore said that the elimination of pores gives rise to the achievement of tensile strength which is just the same as that for the corresponding melt-spun ribbon sample in spite of the significant increase in the sample thickness.

V. Discussion

It is very important to know the cooling rate of the molten alloy in the present high-pressure die casting process. We do not obtain any experimental data on the cooling rate for the bulk La-Al-TM alloys obtained by high-pressure die casting. However, the compositional dependence of the maximum diameter (or thickness) and the critical cooling rate for formation of an amorphous single phase have been examined for the La-Al-TM alloys\textsuperscript{10}. Figure 11 shows the relation between the critical cooling rate (\(R_c\)) and the maximum sample diameter (\(d_c\)) for formation of an amorphous single phase in the La–TM alloys. The data on the critical sample diameter are presented in Table 1 and the critical cooling rate have previously been evaluated\textsuperscript{12} through the experimental data on the change in melting temperature with cooling rate\textsuperscript{13} as well as in glass transition temperature. As shown in Fig. 11, there is a strong correlation for \(d_c\) to increase with a decrease in \(R_c\). The strong relation allows us to evaluate the cooling rate of the molten alloy in the high-pressure die casting process. The cooling rate changes in the range of 55 to 120 K/s in the sample diameter range of 3 to 9 mm. Thus, the cooling rate of the molten alloy is dependent on the diameter of the cast sample. It is generally known that the cooling rate of a
molten alloy in the die casting process increases with an increase in the molten metal pressure and the heat flow at the die-melt interface and with a decrease in the thickness of die lubricant. The present results on the critical sample diameter for formation of an amorphous phase have been obtained in the fixed casting condition and hence the dominant factors on the cooling rate seem to remain unchanged in the present study. Considering that the La–Al–TM alloys with large glass-forming ability have a larger supercooling tendency at a constant cooling condition as compared with the alloys with smaller glass-forming ability, it is not easy to obtain a higher cooling rate exceeding that obtained for the La–Al–TM alloys in the present casting condition.

VI. Summary

The maximum sample thickness for formation of an amorphous single phase by the use of a high-pressure die casting process and the thermal stability and mechanical strength of the resulting bulk amorphous alloys were examined for La–Al–TM (TM = Co, Ni and Cu) alloys. The results obtained are summarized as follows:

1. The maximum diameter for formation of an amorphous single phase in the cylinder samples is 3 mm for La_{55}Al_{25}Ni_{30} and La_{55}Al_{25}Cu_{30}, 7 mm for La_{35}Al_{35}Ni_{30}Cu_{10} and above 9 mm for La_{55}Al_{25}Cu_{10}Ni_{30}Co_{5}. There is a clear tendency for the maximum values to increase with increasing ΔTf.

2. Tg, T1 and ΔHs of the amorphous La_{55}Al_{25}Cu_{10}Ni_{30}Co_{5} sheets are independent of sample diameter in the diameter range of 1 to 9 mm. Furthermore, Tg and ΔHs are just the same as those for the corresponding melt-spin ribbon sample with a thickness of about 20 μm. However, T1 is slightly lower for the cast samples and the deviation is presumably because of the difficulty in the protection of the molten alloy against oxidation.

3. The porosity was measured to be about 20% and the size of the pores was in the range of 2 to 25 μm.

4. The tensile fracture strength (σt) and fracture elongation including elastic elongation (εf) are 700 MPa and 1.5%, respectively, at room temperature. The σt is about 80% as high as that (880 MPa) for the ribbon sample. The difference in σt between the cast cylinder and the melt-spun ribbon is presumably due to the existence of pores. The elimination of pores is expected to give rise to the high tensile strength which is just the same as that for the corresponding melt-spin ribbon.

REFERENCES