Mechanical Properties of Zr-Ti-Al-Ni-Cu Bulk Amorphous Sheets Prepared by Squeeze Casting

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Tensile fracture strength (σ_f) and Vickers hardness (H_v) of Zr-Al-Ni-Cu amorphous sheets with a thickness of 2.5 mm prepared by squeeze casting were found to increase by the addition of 2.5–5 at%Ti and the increase of Al content to 12.5–15 at%. The σ_f and H_v of the amorphous alloy sheets with the new compositions are 1800 to 1850 MPa and 500 to 520, respectively, which are higher than those (σ_f =1650 to 1790 MPa and H_v =470 to 480) for the Zr-10%Al-Ni-Cu amorphous cylinders prepared by copper mold casting. The Young's modulus, elastic elongation and Charpy impact fracture energy are 86 to 92 GPa, 2.0 to 2.2% and 90 to 160 kJ/m², respectively. The highest value of the three point-bending flexural strength is 3900 MPa for Zr₅₅Al₁₅Ni₁₀Cu₂₀. The high impact fracture energy indicates that the cast amorphous alloy sheets have good ductility. Furthermore, the improvement of σ_f and H_v by the simultaneous addition of Ti and Al is presumably due to the increase of the bonding force of the constituent elements resulting from the increase of Zr-Al and Ti-Al pairs with larger negative heats of mixing. The synthesis of the high Al concentration Zr-Al-Ni-Cu and Zr-Ti-Al-Ni-Cu amorphous alloys with higher mechanical strength, higher impact fracture energy and lower density is important for the future progress of high-strength bulk amorphous alloys because the Zr-Al-Ni-Cu amorphous alloys with the 10 at%Al concentration have already been used as new engineering materials.

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I. Introduction

Since bulk amorphous alloys with a wide supercooled liquid region before crystallization were prepared in the Mg-(¹), lanthanide (Ln)-(²) and Zr-based(³)(⁴) alloy systems, their bulk alloys have attracted increasing interest because of the expectation of the development of a new engineering material and the opening-up of a new materials science. Following the above-described nonferrous metal base bulk amorphous alloys, ferrous metal base bulk amorphous alloys in Fe-(Al, Ga)-(P, C, B, Si)(⁵)(⁶), Fe-(Zr, Hf, Nb, Ta)-B(⁷)(⁸) and Fe-Co-(Zr, Nb)-(Mo, W)-B(⁹)(¹⁰) systems have more recently been synthesized. It has subsequently been clarified that these Fe-based bulk amorphous alloys exhibit good soft magnetic properties(¹¹). The maximum sample thickness and the temperature interval of the supercooled liquid region have reached about 10 mm and 67 K, respectively, for the Mg-(¹²) and Ln-based(¹³) alloys, 30 mm(¹⁴) and 127 K(¹⁵) for the Zr-based alloys and 6 mm(⁹) and 89 K(⁸) for the Fe-based alloys. In particular, the Zr-based bulk amorphous alloys exhibit unique mechanical properties which are different from those for conventional crystalline alloys and hence the practical use of their bulk amorphous alloys has been investigated in some application fields such as fine optical machinery parts, writing tools and sporting goods(¹⁶). In order to extend further the application fields of the bulk amorphous alloys, it is important to synthesize a bulk amorphous alloy with higher mechanical strength and lower specific weight in Zr-Al-TM base alloys having the

advantages of easy melting and casting treatments. Inoue *et al.* have previously pointed out(¹⁷) that the addition of a small amount (5 at%) of Ti, Nb or Pd is effective for the increase in the glass formation tendency of arc-melted alloy ingots in Zr-10%Al-Ni-Cu system by the suppression of nucleation of a crystalline phase. Based on the previous information, we have searched for a new Zr-based bulk amorphous alloy with higher specific strength in the Zr-Ti-Al-Ni-Cu system and noticed that Zr₅₅Al₁₅Ni₁₀Cu₂₀, Zr_{52.5}Ti_{2.5}Al₁₅Ni₁₀Cu₂₀ and Zr_{52.5}Ti₅Al_{12.5}Ni₁₀Cu₂₀ bulk amorphous alloys with higher Al concentrations and optimum Ti concentrations exhibit higher tensile strength and lower density as compared with the Zr-10%Al-Ni-Cu bulk amorphous alloys(¹⁸). This paper is intended to present the glass-forming ability, density, mechanical properties and thermal stability of the bulk amorphous Zr-Ti-Al-Ni-Cu alloys and to investigate the influence of additional Al and Ti elements on their properties.

II. Experimental Procedure

Pentenary alloys with composition Zr_{70-x-y}Ti_xAl_yNi₁₀Cu₂₀ ($x=0$ to 12.5 at%, $y=2.5$ to 17.5 at%) were examined in the present study. Their alloy ingots were prepared by arc melting the mixtures of pure Zr, Ti, Al, Ni and Cu metals in an argon atmosphere. The bulk amorphous alloy sheets with a thickness of 2.5 mm, a width of 35 mm and a length of 80 mm were prepared by a squeeze copper mold casting method in an argon atmosphere. Solidification structure was examined by X-

ray diffractometry and optical microscopy. The apparent specific heat was measured by differential scanning calorimetry (DSC) and the stability of the supercooled liquid which appears before crystallization was evaluated from the DSC curves. The ductility of the cast bulk amorphous sheets was evaluated by a hammer test method in which a hammer with a weight of 1.5 kg shown schematically in Fig. 1 was hit at an approximately speed of about 10 m/s. Tensile tests were made with an Instron tensile testing machine at room temperature. The test specimen has the total length of 70 mm and the gauge dimension of 20 mm in length, 2.5 mm in thickness and 3 mm in width. The strain was measured by using a strain gauge and the strain rate was $8.3 \times 10^{-4} \text{ s}^{-1}$. Three points-bending test was also made with an Instron type testing machine. The gauge dimension of the specimen also has the thickness of 2.5 mm, the width of 3 mm and the length of 20 mm. Vickers hardness was measured with a Vickers hardness tester under the load of 9.8 kN.

Fig. 1 Schematic illustration of the hammer impact method to evaluate the ductility of a bulk amorphous alloy sheet with a thickness of 2.5 mm.

As a dynamic mechanical property, the impact fracture energy was measured with a Charpy impact testing machine. The specimen had the gauge shape and dimension which agreed with the No. 3 type JIS criterion. The fracture surfaces after the tensile, bending and impact fracture tests were examined by scanning electron microscopy (SEM). Density was measured by the Archimedian method using a buromethane at 298 K and the accuracy was evaluated to be $\pm 0.005 \text{ Mg/m}^3$.

III. Results

Figure 2 shows the compositional dependence of the cast structure, ductility and density for the $\text{Zr}_{70-x-y}\text{Ti}_x\text{Al}_y\text{Ni}_{10}\text{Cu}_{20}$ amorphous sheets with a thickness of 2.5 mm. The term “ductile” represents that the sheet sample does not fracture after the hammer-impact test, while the “brittle” implies that the sample is fragmented into more than two pieces during the test. It is seen that an amorphous phase is formed in the range of 0 to 10 at%Ti and 5 to 15 at%Al and the ductile-brittle transition occurs in the vicinity of the composition where $x+y=20$ at%, $x \leq 7.5$ and $7.5 \leq y \leq 15$ at%. Figure 2 also shows that the densities of the cast amorphous alloy sheets with good ductility decrease from 6.77 Mg/m^3 for $\text{Zr}_{62.5}\text{Al}_{7.5}\text{Cu}_{20}\text{Ni}_{10}$ to 6.49 Mg/m^3 for $\text{Zr}_{52.5}\text{Ti}_{2.5}\text{Al}_{15}\text{Cu}_{20}\text{Ni}_{10}$ and

Fig. 2 Compositional dependence of density and ductility of cast $\text{Ti}_{70-x-y}\text{Ti}_x\text{Al}_y\text{Ni}_{10}\text{Cu}_{20}$ alloys in a sheet form with a thickness of 2.5 mm.

Table 1 Densities in as-cast amorphous and fully crystallized states and the difference in the densities between the as-cast and crystallized states for cast $\text{Zr}_{70-x-y}\text{Ti}_x\text{Al}_y\text{Ni}_{10}\text{Cu}_{20}$ alloy sheets with a thickness of 2.5 mm.

Alloy	Amorphous state density, $\rho_0/\text{Mg} \cdot \text{m}^{-3}$	Crystallized state density, $\rho/\text{Mg} \cdot \text{m}^{-3}$	$(\rho - \rho_0)/\rho_0$ (%)
$\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$	6.51	6.64	0.5
$\text{Zr}_{57.5}\text{Ti}_{2.5}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$	6.65	6.68	0.3
$\text{Zr}_{55}\text{Ti}_5\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$	6.62	6.64	0.4
$\text{Zr}_{52.5}\text{Ti}_{2.5}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$	6.49	6.52	0.4

6.48 Mg/m³ for Zr₅₀Ti_{7.5}Al_{12.5}Cu₂₀Ni₁₀. Furthermore, **Table 1** summarizes the densities of the as-cast and fully crystallized states for the Zr-Ti-Al-Ni bulk amorphous alloys, together with the difference in densities between the cast bulk amorphous (ρ_0) and crystallized (ρ) samples ($\Delta\rho = (\rho - \rho_0)/\rho_0$). The $\Delta\rho$ values are as small as 0.3 to 0.5% which are much smaller than those (about 2%)⁽¹⁹⁾⁽²⁰⁾ for ordinary amorphous alloys with much higher cooling rates of 10⁴ to 10⁶ K/s for glass formation. The small $\Delta\rho$ values indicate that the bulk amorphous alloys have considerably higher dense random packing density than those for the ordinary amorphous alloys.

Fig. 3 Outer morphology of a cast Zr_{52.5}Ti_{2.5}Al₁₅Ni₁₀Cu₂₀ alloy sheet of 2.5 mm in thickness, 35 mm in width and 80 mm in length prepared by squeeze casting.

Fig. 4 X-ray diffraction pattern and optical micrograph of the cast Zr_{52.5}Ti_{2.5}Al₁₅Ni₁₀Cu₂₀ sheet. The X-ray data of the melt-spun amorphous ribbon are also shown for comparison.

Furthermore, by taking the ease of liquid working into consideration, the Zr_{52.5}Ti_{2.5}Al₁₅Ni₁₀Cu₂₀ alloy was chosen as the most appropriate composition for the purpose of the present study.

Figure 3 shows the outer surface appearance of the cast Zr-Ti-Al-Ni-Cu amorphous sheet with a thickness of 2.5 mm and a width of about 35 mm and a length of 80 mm. The cast sheet has a smooth surface and a good luster. No distinct contrast revealing the precipitation of a crystalline phase is seen over the whole outer surface. In order to confirm the absence of a crystalline phase, an X-ray diffraction pattern of the outer surface and an optical micrograph of the transverse cross section for the cast amorphous sheet are shown in **Fig. 4**, where the X-ray diffraction pattern of the melt-spun amorphous alloy ribbon is also presented for comparison. The diffraction pattern of the cast sheet consists only of broad peaks, in agreement with those for the melt-spun ribbon. Furthermore, no appreciable contrast of a crystalline phase is seen in the cross section. All these results allow to conclude that the cast sheet consists only of an amorphous phase.

Figure 5 shows the DSC curves of the Zr_{70-x}Al_x-Cu₂₀Ni₁₀ and Zr_{70-x-y}Ti_xAl_yCu₂₀Ni₁₀ amorphous alloy

Fig. 5 DSC curves of cast Zr_{70-x}Al_xNi₁₀Cu₂₀ and Zr_{70-x-y}Ti_xAl_yNi₁₀Cu₂₀ amorphous alloy sheets with a thickness of 2.5 mm.

sheets. These alloys exhibit the sequent transition of glass transition, supercooled liquid and crystallization. The temperature interval of supercooled liquid region defined by the difference between glass transition temperature (T_g) and crystallization temperature (T_x), $\Delta T_x (= T_x - T_g)$ is the largest for the 5%Ti-7.5%Al alloy with the single-stage exothermic peak, though the T_g/T_m value is not maximum. This tendency indicates that the stability of the supercooled liquid has a more close relation with the crystallization mode rather than T_g/T_m . Based on the similar DSC curves, Fig. 6(a) shows the compositional dependence of T_g and ΔT_x for the cast bulk amorphous $Zr_{70-x-y}Ti_xAl_yNi_{10}Cu_{20}$ alloys. The T_g increases in the range from 640 K to 715 K with increasing Ti and Al contents, while the ΔT_x shows a maximum value of 110 K for $Zr_{60}Al_{10}Ni_{10}Cu_{20}$ and tends to decrease with deviating al-

loy composition. The large ΔT_x values above 80 K are limited to less than 3 at%Ti and hence the addition of Ti is not preferable for the achievement of the wide supercooled liquid region as compared with Al. Besides, Fig. 6(b) shows the compositional dependence of T_m and T_g/T_m for the $Zr_{70-x-y}Ti_xAl_yNi_{10}Cu_{20}$ amorphous alloy sheets. The T_g/T_m values of the alloys with ΔT_x above 80 K are in the range of 0.57 to 0.62 and the higher T_g/T_m values of 0.64 and 0.65 are obtained for the alloys with smaller ΔT_x values. As is the case shown in Fig. 5, the ΔT_x does not always have a close relation to T_g/T_m for the Zr-Ti-Al-Cu-Ni amorphous alloys.

Figure 7(a) shows the compositional dependence of the tensile fracture strength (σ_f) and Vickers hardness (H_v) for the $Zr_{70-x-y}Ti_xAl_yNi_{10}Cu_{20}$ amorphous alloy sheets. The H_v tends to increase from 480 to 520 with increasing Ti and Al contents, while the σ_f also shows the

Fig. 6 Compositional dependence of (a) glass transition temperature (T_g) and temperature interval of supercooled liquid region ($\Delta T_x (= T_x - T_g)$), and (b) melting temperature (T_m) and reduced glass transition temperature (T_g/T_m) for cast $Zr_{70-x-y}Ti_xAl_yNi_{10}Cu_{20}$ amorphous alloy sheets.

Fig. 7 Compositional dependence of (a) tensile fracture strength (σ_f) and Vickers hardness (H_v), and (b) specific tensile strength defined by the ratio of σ_f to density (ρ) for cast $Zr_{70-x-y}Ti_xAl_yNi_{10}Cu_{20}$ amorphous alloy sheets.

similar dependence in the Ti content up to about 5 at% and the higher σ_f values above 1800 MPa are obtained in the higher Ti and Al concentration range. However, in the Ti concentration range above 6 at%, the σ_f decreases significantly in spite of the increase in H_v . The inconsistency between σ_f and H_v in the higher Ti concentration range seems to result from the decrease of ductility for the cast amorphous alloy sheets. Based on the data on the density and σ_f shown in Figs. 2 and 7(a), respectively, the compositional dependence of the specific tensile strength defined by the ratio of σ_f to density (ρ), σ_f/ρ , for the Zr-Ti-Al-Cu-Ni amorphous alloy sheets is shown in Fig. 7(b). The high specific strength reaching about 28×10^5 Nm/kg is obtained for the 2.5%Ti-15%Al and 5%Ti-12.5%Al alloys. This results indicate clearly that the simultaneous addition of optimum amounts of Ti and Al elements is useful for the increase of the specific strength for the Zr-based bulk amorphous alloys.

Figure 8 shows the tensile stress-strain curve and fracture surface appearance of the cast $\text{Zr}_{52.5}\text{Ti}_{2.5}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$ amorphous alloy sheet. Although no appreciable plastic elongation is recognized in the tensile stress-elongation curve, the sample has a large elastic elongation limit of about 2.2% and a Young's modulus of 92 GPa. The tensile fracture takes place along the maximum shear plane which is declined by about 45 degrees to the direction of tensile load and the fracture surface consists of a small part of smooth region and a dominant part of vein region. The dominant vein region is shown in Fig. 8. These results indicate that the deformation and fracture take place by a small amount of inhomogeneous shear sliding, followed by an adiabatic instantaneous fracture, because of the non-strain hardening characteristic of an

amorphous alloy⁽²¹⁾.

Figure 9 summarizes the relation between tensile fracture strength and Young's modulus for the cast $\text{Zr}_{70-x-y}\text{Ti}_x\text{Al}_y\text{Cu}_{20}\text{Ni}_{10}$ amorphous alloy sheets with a thickness of 2.5 mm. There is a clear tendency for σ_f to increase with increasing Young's modulus, in agreement with those for the other Zr-based alloys in melt-spun ribbon and cast cylindrical forms. The ratio of σ_f to E is evaluated to be 0.024 which is much higher than that (0.007)⁽²²⁾ for ordinary crystalline alloys. The significant

Fig. 9 Relation between σ_f and Young's modulus (E) for the cast amorphous $\text{Zr}_{70-x-y}\text{Ti}_x\text{Al}_y\text{Ni}_{10}\text{Cu}_{20}$ alloys.

Fig. 8 Tensile stress-strain curve and tensile fracture surface appearance of the cast amorphous $\text{Zr}_{52.5}\text{Ti}_{2.5}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$ sheet.

Fig. 10 Bending flexural stress-deflection curves of the bulk amorphous $Zr_{70-x-y}Ti_xAl_yNi_{10}Cu_{20}$ sheets with a thickness of 2.5 mm.

difference indicates clearly that the bulk amorphous alloys have the features of higher tensile strength and lower Young's modulus which are distinguished from those for ordinary crystalline alloys.

We also measured the three-points bending strength of the cast bulk amorphous alloy sheets. Figure 10 shows bending flexural stress-deflection curves of the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$, $Zr_{55}Ti_5Al_{10}Ni_{10}Cu_{20}$ and $Zr_{52.5}Ti_{2.5}Al_{15}Ni_{10}Cu_{20}$ amorphous alloy sheets subjected to the three-points bend test at room temperature. By applying the load at three points and causing bending, a tensile force acts on the material opposite the midpoint. Fracture begins at this location. The flexural strength ($\sigma_{b,f}$) and flexural modulus ($E_{b,f}$) are evaluated by the following relations (1) and (2), respectively⁽²³⁾.

$$\sigma_{b,f} = (3FL) / (2wh^2) \quad (1)$$

$$E_{b,f} = (L^3F) / (4wh^3\delta) \quad (2)$$

Here, F is the fracture load, L is the distance between the two outer points, w is the width of the specimen, h is the height of the specimen, and δ is the deflection of the beam up to fracture. The $\sigma_{b,f}$, $E_{b,f}$ and δ are evaluated to be as high as 2930 MPa, 92 GPa and 2.4 mm, respectively, for the $Zr_{55}Ti_5Al_{10}Ni_{10}Cu_{20}$ sheet, 3895 MPa, 115 GPa and 2.5 mm, respectively, for the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ sheet and 3300 MPa, 104 GPa and 2.1 mm, respectively, for the $Zr_{52.5}Ti_{2.5}Al_{15}Ni_{10}Cu_{20}$ sheet. The bending flexural strength is about 1800 to 1900 MPa for the bulk amorphous $Zr_{60}Al_{10}Ni_{10}Cu_{20}$ alloy prepared by the conventional copper mold casting method or by the extension of atomized amorphous powders in the supercooled liquid

region (powder metallurgy method)⁽²⁴⁾. It is therefore concluded that the squeeze casting method is useful for the production of Zr-based bulk amorphous alloys with much higher bending flexural strength. Table 2 summarizes the Charpy impact fracture energy (E_f) of the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$, $Zr_{55}Ti_5Al_{10}Ni_{10}Cu_{20}$ and $Zr_{52.5}Ti_{2.5}Al_{15}Ni_{10}Cu_{20}$ amorphous sheets, together with the tensile fracture strength, Young's modulus, bending flexural strength, flexural modulus and deflection of the same sheet samples. The Charpy impact fracture energies are 83 to 160 kJ/m² which are about 1.5 to 2.5 times as high as those (68 to 70 kJ/m²) for the bulk amorphous Zr-Al-Ni-Cu⁽²⁴⁾⁽²⁵⁾ and Pd-Cu-Ni-P⁽²⁶⁾ alloy sheets prepared by the conventional copper mold casting method without applied squeeze force. The significant improvement of the Charpy impact fracture energy is presumably because the bulk alloy sheets prepared by the squeeze cast method can contain a significant amount of compressive residual stress in the outer surface region⁽²⁷⁾.

IV. Discussion

1. The difference in compositional dependence between ΔT_x and T_g/T_m

The ΔT_x shows the largest value of 110 K for the $Zr_{60}Al_{10}Ni_{10}Cu_{20}$ alloy and decreases significantly with deviating alloy composition, particularly, with increasing Ti content. The ΔT_x value is below 80 K in the Ti concentration range above 5 at%. However, the higher T_g/T_m values above 0.63 are obtained for the $Zr_{60-x}Ti_xAl_{10}Cu_{20}Ni_{10}$ alloys containing 5 and 7.5%Ti. Thus, one cannot see a tendency for ΔT_x to increase with increasing T_g/T_m . This is inconsistent with the previous tendency for ΔT_x to increase with increasing T_g/T_m . It has also been pointed out⁽¹⁶⁾⁽²⁸⁾⁻⁽³⁰⁾ that the ΔT_x is dominated by the crystallization mode and the single-stage crystallization mode for the multicomponent amorphous alloys induces the larger ΔT_x value. The high T_g/T_m implies that the viscosity of the supercooled liquid increases steeply with decreasing temperature. It is known⁽²²⁾⁽³¹⁾ that the steep increase in viscosity is one of the dominant factors for the achievement of high glass-forming ability. On the other hand, the single-stage crystallization mode implies the simultaneous precipitation of multiple crystalline phases which requires the long-range atomic rearrangement of the constituent elements. The long-range atomic rearrangements are difficult for the present multicomponent amorphous alloys with the higher dense random packing density, resulting in the large ΔT_x values. It has previously been reported⁽¹⁶⁾⁽²⁸⁾⁻⁽³⁰⁾ that the higher packing

Table 2 Charpy impact fracture energy and static mechanical properties of cast $Zr_{70-x-y}Ti_xAl_yNi_{10}Cu_{20}$ alloy sheets.

Alloy	σ_t / MPa	E / GPa	H_v	$\sigma_{b,f}$ / MPa	$E_{b,f}$ / GPa	δ / mm	E_f / kJ·m ⁻²
$Zr_{55}Al_{15}Ni_{10}Cu_{20}$	1850	90	520	3894	115	2.5	160
$Zr_{55}Ti_5Al_{10}Ni_{10}Cu_{20}$	1600	86	510	2930	92	2.4	96
$Zr_{52.5}Ti_{2.5}Al_{15}Ni_{10}Cu_{20}$	1800	92	520	3300	104	2.1	83

density comes from the satisfaction of the following three factors, *i.e.*, (1) multicomponent system consisting of more than three elements, (2) significant difference in atomic size above about 12% among the main three constituent elements, and (3) negative heats of mixing among their elements. The degree of the satisfaction of the three empirical rules is thought to increase by the addition of Ti as well as by the optimization of Al concentration.

2. The increases in σ_f and H_v by the addition of Ti and Al

It was shown in Figs. 6 and 7 that the mechanical strength increases by the addition of Ti less than about 5 at% and by the increase of Al content from 10% to 15 at% in the maintenance of large ΔT_x values above 70 K. The higher values of σ_f and H_v are obtained for the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$, $Zr_{52.5}Ti_{2.5}Al_{15}Ni_{10}Cu_{20}$ and $Zr_{52.5}Ti_{5.5}Al_{12.5}Ni_{10}Cu_{20}$ alloys containing larger amounts (15 to 17.5 at%) of Ti and Al elements as compared with the ordinary $Zr_{60-62.5}Al_{7.5-10}Ni_{10}Cu_{20}$ alloy. It is presumed that the addition of Ti and the increase in Al content induce the generation of new atomic bonding pairs of Ti–Al and Ti–TM with large negative heats of mixing⁽³²⁾ as well as the increase of the numbers of the atomic bonding pairs of Zr–Al and Al–TM. These changes in the atomic pairs are favorable for the increases in σ_f and H_v in the maintenance of good ductile nature. The increases in σ_f and H_v combined with the decrease in density are important for further development of the Zr-based bulk amorphous alloys as a high-strength engineering material.

3. Improvement of bending flexural strength and Charpy impact fracture energy by the squeeze casting method

It has previously been reported⁽²⁴⁾⁽²⁵⁾ that the $\sigma_{b,f}$ and E_f are 1800 to 1900 MPa and 70 to 80 kJ/m², respectively, for the $Zr_{60}Al_{10}Ni_{10}Cu_{20}$ bulk amorphous alloys with a cylindrical form prepared by the conventional copper mold casting method. The similar values of $\sigma_{b,f}$ and E_f have also been reported for the bulk amorphous alloy prepared by the powder metallurgy method consisting of extrusion of atomized amorphous powders in the supercooled liquid region⁽²⁴⁾. In comparison with the previous data on the $\sigma_{b,f}$ and E_f , one can notice that the $\sigma_{b,f}$ and E_f for the present bulk amorphous alloys prepared by squeeze casting are much higher and the difference reaches as large as 1.5 to 2.5 times. It is generally known⁽³³⁾ that the bending flexural strength and the bending fracture energy for oxide glasses are very sensitive to the residual stress condition and the existence of the residual compressive stress in the outer surface region induces significant increases in $\sigma_{b,f}$ and E_f . Furthermore, the residual compressive stress in the outer surface region can be introduced by the quenching⁽³³⁾. The quenching treatment has been used as an effective strengthening method of oxide glasses. Furthermore, the existence of the residual compressive stress is effective for the increases in the bending flexural strength and bending fatigue strength and no significant increase in tensile fracture strength has

been recognized presumably because of a preferential initiation of crack in the inner region having residual tensile stress. In the present squeeze casting method, a much higher cooling rate is achieved in the outer surface region of the metallic liquid because of the direct contact with copper mold. The significant difference in the cooling rate between the outer surface region and the inner region induces the generation of the residual compressive stress in the outer surface region and the residual tensile stress in the inner region. The residual compressive stress can yield the increase in the bending flexural strength to about 4000 MPa which is about 2 times higher than that (about 1800 to 1900 MPa) for the ordinary bulk amorphous alloys in which a compressive residual stress is not included in the outer surface region.

V. Conclusions

With the aim of developing a new Zr-based bulk amorphous alloy, we examined the effect of Ti and Al concentrations on the thermal stability and mechanical properties of cast bulk amorphous Zr–Ti–Al–Ni–Cu alloy sheets with a thickness of 2.5 mm prepared by the squeeze casting method. As a result, the increase in Al content to 15 at% and the addition of Ti up to 5 at% were found to be effective for the increases in tensile strength (σ_f), bending flexural strength ($\sigma_{b,f}$) and Vickers hardness (H_v). The σ_f , $\sigma_{b,f}$, H_v and Charpy impact fracture energy are 1850 MPa, 3895 MPa, 520 and 160 kJ/m², respectively, for the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ sheet and 1800 MPa, 3300 MPa, 520 and 90 kJ/m² for the $Zr_{52.5}Ti_{2.5}Al_{15}Ni_{10}Cu_{20}$ sheet. The density decreases from 6.68–6.77 Mg/m³ for the previously reported $Zr_{90-x}Al_{10}TM_x$ amorphous alloys to 6.49–6.51 Mg/m³ and leads to the increase in the specific strength from $24\text{--}26 \times 10^5$ to 28×10^5 N·m/kg. The effectiveness of the additional Al and Ti elements is presumably due to the increase of the bonding force among the constituent elements by the increases of Ti–Al and Zr–Al pairs with larger negative heats of mixing. Now that the Zr–Al–TM amorphous alloys have already been used as engineering materials with high strength and good ductility, the fabrication of the Zr–Ti–Al–Ni–Cu and high Al concentration Zr–Al–Ni–Cu bulk amorphous alloys with the higher specific strength, higher impact fracture energy and higher T_g/T_m values by the squeeze casting process may be a bright prospect for development of bulk amorphous alloys.

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