Zr–Al–Ni Amorphous Alloys with High Glass Transition Temperature and Significant Supercooled Liquid Region

By Akihisa Inoue*, Tao Zhang** and Tsuyoshi Masumoto*

Amorphous Zr–Al–Ni alloys exhibiting a wide temperature region of supercooled liquid state and a high reduced glass transition temperature \( (T_g/T_m) \) were formed over a composition range from 0 to 37 at% Al and 3 to 67% Ni by melt spinning. The temperature span \( \Delta T_g (T_g - T_m) \) between \( T_g \) and crystallization temperature \( T_m \) reaches as large as 77 K for Zr65Al15Ni10. The \( T_g/T_m \) is also as high as 0.64 in the vicinity of Zr64Al16Ni8 and their Zr–Al–Ni alloys are concluded to have a large glass-forming capacity. The \( T_g \) and hardness \( (H_g) \) increase with increasing Al and Ni contents in the range from 660 to 860 K and 400 to 720, respectively, and the tensile strength also has a similar compositional dependence in the range of 1335 to 1720 MPa. The compositional effect on \( T_g \) and \( H_g \) was presumed to originate from the variation of the atomic configuration which reflects the equilibrium compounds, because of the similarity in the compositional dependence among \( T_g \), \( H_g \), and the melting temperature of the compounds. The high thermal stability of the supercooled liquid in the vicinity of Zr6AlNi, seems to result from optimum bonding and packing states of the constituent atoms in the limited alloy.

Received December 15, 1990

Keywords: zirconium-aluminum-nickel alloy, amorphous phase, supercooled liquid, glass transition, reduced glass transition temperature, glass-forming ability, melt spinning

1. Introduction

It is known that oxide and fluoride glasses exhibit a wide supercooled liquid region before crystallization and the high stability of the glassy structure in the supercooled liquid region results in good deformability of their glasses into a given shape and high glass-forming capacity which enable us to use as practical materials in a number of fields. On the other hand, no glass transition phenomenon has been observed in a majority of metallic amorphous alloys. The appearance of a wide supercooled liquid region before crystallization had been limited, for the last two decades, to Pt- and Pd-based amorphous alloys in the Pt–Ni–P, Pd–Ni–P, Pd–Cu–Si and Pd–Ni–Si systems\(^{(1)}\). Recently, Inoue et al. have reported that the lanthanide–Al base amorphous alloys such as La–Al–Ni\(^{(2)}\) and La–Al–Cu\(^{(3)}\) exhibit a wide supercooled liquid region comparable to that for Pt–Ni–P amorphous alloys. If an amorphous alloy with a wide supercooled liquid is found in an alloy system consisting mainly of transition metals without noble and lanthanide metals, usefulness of amorphous alloys as practical materials is expected to increase significantly because of some advantages of good deformability in the supercooled liquid, amorphization at a low cooling rate and in air or water and so forth. In a subsequent searching of amorphous alloys exhibiting a wide supercooled liquid region in alloy systems without noble and lanthanide metals, the present authors have found that Zr–Al–M (M=Mn, Fe, Co, Ni or Cu) ternary amorphous alloys exhibit a wide supercooled liquid region and the temperature interval between glass transition temperature \( (T_g) \) and crystallization temperature \( (T_m) \), \( \Delta T_g (T_g - T_m) \) reaches about 90 K which exceeds largely those (60–70 K) for Pt–Ni–P\(^{(4)}\) and La–Al–Ni\(^{(5)}\) amorphous alloys. The present paper is intended to present the composition range where an amorphous phase with a wide supercooled liquid region is obtained in rapidly solidified Zr–Al–Ni alloys and thermal stability and mechanical properties of the amorphous alloys.

II. Experimental Procedure

Ternary Zr–Al–Ni alloys were used in the present study. Their ingots were prepared by arc melting a mixture of pure Zr (99.9 mass%), Al (99.99 mass%) and Ni (99.9 mass%) metals in a purified argon atmosphere. The compositions are nominally expressed in atomic per cent. From the master alloy ingots, ribbons with a cross section of about 0.03 mm × 1 mm were prepared by a single roller melt-spinning technique in an argon atmosphere. The amorpicity of the melt-spun ribbons was examined by X-ray diffraction and transmission electron microscopy techniques.

The specific heat \( (C_p) \) associated with structural relaxation, glass transition and crystallization was measured with a differential scanning calorimeter (DSC). The accuracy of the data was about ±0.4 J/mol·K for absolute \( C_p \) values and better than ±0.1 J/mol·K for the relative \( C_p \) or \( \Delta C_p \) measurements. The samples were first scanned at 0.67 K/s (40 K/min) to the temepature of the super-
cooled liquid to obtain data in the as-quenched state, and then cooled to room temperature. The $C_p(T)$ measurement was immediately repeated in situ to obtain data on the control sample. This test procedure is essential in order to eliminate any possible error that might result from the drift in the calorimeter between the measurements. Hardness and tensile strength of the ribbon specimens were measured by a Vickers microhardness tester with a 0.98 N (100 g) load and an Instron-type tensile testing machine at a strain rate of $4.17 \times 10^{-4}$ s$^{-1}$, respectively. Eight to ten symmetrical indentations and five tensile test data were used to determine the average microhardness value and tensile fracture strength. Tensile specimens were cut from the melt-spun ribbon into strips having a gauge dimension of 20 mm long for fracture strength. Subsequent to tensile testing, the cross-sectional area at the fracture site of each specimen was measured by optical or scanning electron microscopy in order to minimize error in the estimation of the tensile strength. The melting temperature of the as-cast ingots and melt-spun ribbons was measured at a scanning rate of 0.33 K/s (20 K/min) with a differential thermal analyzer (DTA).

III. Results

Figure 1 shows the composition range in which an amorphous Zr–Al–Ni phase is formed by melt spinning, along with the data of bending ductility of the amorphous alloys. The glass formation range is quite wide and can be divided into two categories of Zr-rich and Al-rich compositions; 0 to 37 at% Al and 3 to 67% Ni for the Zr-rich alloys and 55 to 88% Al and 7 to 33% Ni for the Al-rich alloys. In addition, it is seen in Fig. 1 that binary amorphous alloys are formed in 18 to 70% Ni for the Zr–Ni system, being consistent with the previous data on the glass formation range. It is thus notable that the Zr–Al–Ni alloys can be amorphpized over a wide compositional range which is comparable to about 30 to 40% in area in the entire compositional range of the ternary system. Figure 1 also shows that ductile amorphous alloys, which can be bent through 180 degrees without fracture, are obtained in the Zr-rich range of 0 to 37% Al and 3 to 65% Ni and in the Al-rich range of 81 to 88% Al and 7 to 12% Ni. One can see a tendency that an approach of alloy composition to Zr$_3$Al$_{70}$Ni$_{30}$ brings about the transition from ductile to brittle nature of the Zr–Al–Ni amorphous alloys.

Figure 2 shows the compositional dependence of crystallization temperature ($T_c$) for the Zr–Al–Ni amorphous alloys. The $T_c$ value is in the range of 660 to 740 K for the Zr-rich alloys containing about 75% Zr, increases significantly with increasing Al and Ni contents and exceeds 860 K for Zr$_{40}$Al$_{10}$Ni$_{50}$. With a further increase in Al content for the Zr–Al–Ni system, $T_c$ decreases significantly to 475 K for Zr$_{55}$Al$_{25}$Ni$_{20}$. As is evident from the contour lines of $T_c$ in Fig. 2, the $T_c$ value of the Zr–Al–Ni amorphous alloys is dominated by Al and Ni contents and tends to exhibit a maximum in the vicinity of Zr$_3$Al$_{70}$Ni$_{30}$.

As an example, Fig. 3 shows the DSC curves of Zr$_{55}$Al$_{10}$Ni$_{35}$, (x = 25, 30 and 35 at%) amorphous alloys. It is seen that the three alloys crystallize through a single stage accompanied by an exothermic heat ($\Delta H_c$) ranging from 2.44 to 4.23 kJ/mol. In addition to the exothermic peak, one can notice an endothermic reaction with a very wide temperature span in the temperature range below the onset temperature ($T_{on}$) of crystallization for the three amorphous alloys. For instance, the Zr$_{55}$Al$_{30}$Ni$_{15}$ amorphous alloy begins to transform from the amorphous solid to a supercooled liquid at about 754 K and keeps the supercooled liquid state in a wide temperature span reaching about 60 K, followed by crystallization at 814 K.
Considering the previous data\(^5\) that the highest \(T_a\) value in noble and lanthanide metal base amorphous alloys is 688 K for Pd–Ni–Si system, it is notable that the \(T_a\) values of the Zr–Al–Ni amorphous alloys are much higher than that of the amorphous alloys exhibiting the glass transition phenomenon. It is also seen in Fig. 3 that the \(\Delta H_k\) value is larger for the Zr\(_{55}\)Al\(_{20}\)Ni\(_{25}\) alloy with a larger \(\Delta T_s\) value.

Figure 4 shows the compositional effect on the \(\Delta T_s\) value for the Zr–Al–Ni amorphous alloys. The \(\Delta T_s\) value has a maximum value of 77 K for Zr\(_{50}\)Al\(_{15}\)Ni\(_{35}\) and decreases with a deviation from the alloy component. However, it is notable that the \(\Delta T_s\) value above 50 K is obtained in the wide composition range from 7 to 24\%Al and 13 to 32\%Ni. Considering previous data that the large \(\Delta T_s\) value reported up to date is about 70 K for Pt–Ni–P\(^4\), 65 K for Pd–Ni–P\(^7\), 58 K for Mg–Ni–La\(^8\), 69 K for La\(_{80}\)Al\(_{20}\)Ni\(_{12}\)\(^2\) and 59 K for La\(_{80}\)Al\(_{23}\)Cu\(_{3}\)\(^3\), it is believed that the Zr\(_{50}\)Al\(_{15}\)Ni\(_{35}\) alloy has the largest \(\Delta T_s\) value in all metallic amorphous alloys. With the aim of confirming the relation between \(\Delta T_s\) and \(\Delta H_k\) shown in Fig. 3, the compositional dependence of the \(\Delta H_k\) was examined for the Zr–Al–Ni amorphous alloys. As shown in Fig. 5, the \(\Delta H_k\) is maximum in the vicinity of Zr\(_{55}\)Al\(_{15}\)Ni\(_{30}\) and tends to decrease with a deviation from the composition. This compositional dependence agrees well with that for the \(\Delta T_s\) and there is a strong correlation between \(\Delta T_s\) and \(\Delta H_k\).

In order to examine the change of the specific heat by the transition of an amorphous solid to a supercooled liquid and the temperature dependence of the specific heat in the amorphous solid and supercooled liquid, the detailed differential scanning calorimetric measurement was made for the Zr–Al–Ni amorphous alloys. As an example, Fig. 6 shows the thermograms of an amorphous Zr\(_{60}\)Al\(_{15}\)Ni\(_{25}\) alloy with the widest supercooled liquid region. The \(C_p\) value of the as-quenched phase is 23.9 J/mol·K near room temperature. As the temperature rises, the \(C_p\) value increases gradually and begins to decrease, indicating an irreversible structural relaxation at about 440 K. With a further increase in temperature, the \(C_p\) value reaches its minimum at about 640 K, then increases rapidly in the glass transition range from 660 to 720 K and reaches 33.7 J/mol·K for the supercooled liquid around 730 K. With further increased temperature, the \(C_p\) value of the supercooled liquid decreases gradually and then rapidly due to crystallization at 770 K. It is
seen in Fig. 6 that the transition of the amorphous solid to the supercooled liquid occurs accompanied by a large increase in the specific heat, $\Delta C_{p,s\rightarrow l}$, of 6.25 J/mol·K. The difference in $C_p(T)$ between the as-quenched and the reheated states, $[\Delta C_p(T)]$, manifests the irreversible structural relaxation which is presumed to arise from the annihilation of various kinds of quenched-in “defects” and the enhancement of the topological and chemical short-range ordering through the atomic rearrangement. The details of the structural relaxation behavior will be described elsewhere.

The $C_{p,s}$ curve of the reheated (control) sample is unaffected by thermal changes and consists of configurational contributions as well as those arising from purely thermal vibrations. Therefore, the vibrational specific heat, $C_{p,v}$, for the amorphous alloy is extrapolated from $C_p$ values in the low temperature region and is a linear function of temperature, viz,

$$C_{p,v} = 23.9 + 1.29 \times 10^{-2}(T - 340) \quad 340 \leq T \leq 620 \quad (1)$$

Similarly, the equilibrium specific heat, $C_{p,e}$, of the supercooled liquid, including the vibrational and configurational specific heat, can be expressed by eq. (2) based on the data shown in Fig. 6,

$$C_{p,e} = 33.7 + 2.59 \times 10^{-2}(755 - T) \quad 735 \leq T \leq 760 \quad (2)$$

The $\Delta C_{p,s\rightarrow l}$ value for the Zr-Al-Ni amorphous alloys was examined as a function of composition. As a result, it was found that the $\Delta C_{p,s\rightarrow l}$ value is about 6.5 J/mol in the vicinity of Zr$_{60}$Al$_{30}$Ni$_{10}$ and tends to decrease with a deviation from the alloy composition, being similar to the compositional dependence of $\Delta T_s$ and $\Delta H_v$. That is, there is a tendency that the larger the $\Delta T_s$ and $\Delta H_v$, the larger is the $\Delta C_{p,s\rightarrow l}$. However, the $\Delta C_{p,s\rightarrow l}$ values are considerably smaller than those (10 to 20 J/mol·K) for Pt-Ni-P, Pd-Ni-P, Mg-Ni-La, La-Al-Ni, and La-Al-Cu amorphous alloys. Although the reason for the small $\Delta C_{p,s\rightarrow l}$ value remains unknown, it may be related to the result that the glass transition appears at temperatures much higher than the $T_v$ values of the Pt-, Pd-, Mg- and La-based amorphous alloys.

It is important to examine the reduced glass transition temperature ($T_v/T_m$) for the Zr-Al-Ni amorphous alloys exhibiting the wide supercooled liquid region. As exemplified for Zr$_{60}$Al$_{15}$Ni$_{25}$ in Fig. 7, the onset temperature of fusion can be accurately measured from the DTA curve. When the onset temperature of the endothermic reaction in the temperature range above $T_s$ is regarded as a melting temperature ($T_m$), the $T_v/T_m$ value is evaluated to be 0.64 in the vicinity of 20%Al and 20%Ni exhibiting a wide supercooled liquid region and decreases gradually with a deviation from the composition, e.g., 0.63 for

![Fig. 6](image-url)  
**Fig. 6** The thermogram $C_{p,s}(T)$ of an amorphous Zr$_{60}$Al$_{15}$Ni$_{25}$ alloy in the as-quenched state. The solid line represents the thermogram $C_{p,s}(T)$ of the sample heated to 750 K.

![Fig. 7](image-url)  
**Fig. 7** Differential thermal analytical (DTA) curves of a Zr$_{60}$Al$_{15}$Ni$_{25}$ amorphous alloy.

![Fig. 8](image-url)  
**Fig. 8** Compositional dependence of Vickers hardness number ($H_v$) of Zr-Al-Ni amorphous alloys.
Table 1  Mechanical properties of Zr-Al-Ni amorphous alloys.

<table>
<thead>
<tr>
<th>Alloy (at%)</th>
<th>$\sigma_i$ (MPa)</th>
<th>$E$ (GPa)</th>
<th>$H_e$, $\varepsilon_{e,t} = \sigma_i/E$</th>
<th>$\varepsilon_{e,t} = 9.8$</th>
<th>$\sigma_{e,t} = 9.8 H_e/3$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$<em>2$Al$</em>{19.28}$Ni$_{71.72}$</td>
<td>1335</td>
<td>60.0</td>
<td>432</td>
<td>0.021</td>
<td>0.023</td>
</tr>
<tr>
<td>Zr$<em>2$Al$</em>{19.25}$Ni$_{71.75}$</td>
<td>1520</td>
<td>64.5</td>
<td>484</td>
<td>0.024</td>
<td>0.024</td>
</tr>
<tr>
<td>Zr$<em>2$Al$</em>{19.3}$Ni$_{71.7}$</td>
<td>1640</td>
<td>70.5</td>
<td>494</td>
<td>0.023</td>
<td>0.023</td>
</tr>
<tr>
<td>Zr$<em>2$Al$</em>{19.3}$Ni$_{71.7}$</td>
<td>1715</td>
<td>72.6</td>
<td>502</td>
<td>0.024</td>
<td>0.024</td>
</tr>
<tr>
<td>Zr$<em>2$Al$</em>{19.28}$Ni$_{71.72}$</td>
<td>1720</td>
<td>78.2</td>
<td>549</td>
<td>0.022</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Tensile fracture strength ($\sigma_{e,t}$), Young’s modulus ($H_e$), Vickers hardness ($H_e$), tensile fracture strain ($\varepsilon_{e,t} = \sigma_i/E$), compressive yield strain ($\varepsilon_{c,t} = 9.8 H_e/3$) and compressive yield strength ($\sigma_{c,t} = 9.8 H_e/3$).

Zr$_{35}$Al$_{38}$Ni$_{27}$ and 0.60 for Zr$_{60}$Al$_{15}$Ni$_{25}$. There is a clear tendency that the higher the $T_s / T_m$ value, the larger are the $\Delta T_s$ and $\Delta C_p = 1$.

Vickers hardness ($H_e$) and tensile fracture strength ($\sigma_i$) were measured for the ductile Zr-Al-Ni amorphous alloys exhibiting large values of $\Delta T_s$, $\Delta C_p = 1$, and $T_s / T_m$. Figure 8 shows the compositional effect on the $H_e$ for the Zr-Al-Ni amorphous alloys. The $H_e$ value is about 400 in the vicinity of 5% Al and 25% Ni, increases significantly with increasing Al and Ni contents and reaches a maximum value of 720 in the vicinity of 30% Al and 30% Ni. Thus, the increase of the $H_e$ value with an increase of Al and Ni contents is more remarkable in the condition of Al/Ni = 1.0. The feature of the compositional effect on $H_e$ is very analogous to those for $T_s$ and $T_m$.

A similar compositional effect was also recognized for the tensile fracture strength ($\sigma_i$) and Young’s modulus ($E$). As summarized in Table 1, the $\sigma_i$ and $E$ values increase with increasing Al and Ni contents from 1335 and 1720 MPa and 61.0 to 78.2 GPa, respectively. Furthermore, it is seen that the $\varepsilon_{e,t}$ evaluated from the ratio of $\sigma_i/E$ exceeds 0.02 and the $\sigma_i$ and $\varepsilon_{e,t}$ values are nearly equal to the $\sigma_{e,t}$ and $\varepsilon_{c,t}$, respectively, indicating that the Zr-Al-Ni amorphous alloys have a rather good ductile nature. Here, it is important to point out that the high stability of the supercooled liquid ($\Delta T > 70$ K), the high reduced glass transition temperature ($T_s/T_m > 0.60$) and the high strengths ($\sigma_i > 1700$ MPa and $E > 65$ GPa) are satisfied simultaneously for some amorphous alloys in the Zr-Al-Ni system.

IV. Discussion

1. Compositional effect on $T_s$, $H_e$, $E$ and $\sigma_i$

It was shown in section III that the $T_s$, $H_e$, $E$ and $\sigma_i$ values of the Zr-Al-Ni amorphous alloys have the same compositional effect and increase with increasing Al and Ni contents. The maximum values of $T_s$, $H_e$, $E$ and $\sigma_i$ are obtained in the vicinity of Zr$_2$Al$_3$Ni$_{10}$ and the increase in $T_s$, $H_e$, $E$ and $\sigma_i$ is the largest when the concentration ratio of Al to Ni is nearly 1.0. Although the atomic configuration in the Zr-Al-Ni amorphous alloys remains unclear, it is interpreted that the simultaneous existence of the solute elements (Al and Ni) in the Zr-based amorphous alloys brings about the increase in $T_s$, $H_e$, $E$ and $\sigma_i$. Although there is no equilibrium phase diagram available in the Zr-Al-Ni ternary alloy, the binary phase diagrams of Zr-Al$^{90}$ and Zr-Ni$^{90}$ alloys indicate that the increase in $T_s$, $H_e$, $E$ and $\sigma_i$ coincides well with the significant increase in the $T_m$ from 1623 to 1805 K for the Zr-Al system and from 1233 to 1533 K for the Zr-Ni system, accompanied by the structural changes of Zr$_3$Al$_2$+Zr$_3$Al$_5$→Zr$_3$Al$_3$→Zr$_3$Al$_3$+Zr$_2$Ni→Zr$_2$Ni→Zr$_2$Ni→Zr$_2$Ni→Zr$_2$Ni→Zr$_2$Ni. Although the amorphous structure of the Zr-Al-Ni alloys is under investigation, the previous data allow us to presume that the atomic configuration on a short-range scale varies with the subsequent change in the equilibrium compounds. That is, the amorphous structure reflects the Zr$_2$Al$_3$, Zr$_2$Al$_5$ and Zr$_2$Ni with low $T_m$ in the Zr-rich compositional range and the increase in the Al and Ni contents gives the variation into the amorphous structure which reflects the Zr$_2$Al$_3$ (or Zr$_2$Al$_5$)+ZrNi and ZrAl+ZrNi compounds with higher $T_m$. Accordingly, the monotonous and significant increases in $T_s$, $H_e$, $E$ and $\sigma_i$ with increasing Al and Ni contents may be explained by the variation of the short-range atomic configuration which reflects the change of their equilibrium compounds. It is expected from a common concept for the solid solution that the achievement of the entire replacement gives the maximum values of $T_s$ and $H_e$ in the compositional range where the concentration ratio of Al to Ni is nearly 1.0. Furthermore, the attractive bonding nature between Al and Ni atoms is thought to play an important role in the increase in $T_s$, $H_e$, $E$ and $\sigma_i$ with increasing Al and Ni contents. The attractive bonding nature is also expected to be the largest in the vicinity of Al/Ni = 1.0, because of the highest $T_m$ value at 50% Ni in Al-Ni binary system. The compositional effect of the attractive bonding nature between Al and Ni is presumed to bring about the compositional dependence in which the $T_s$ and $H_e$ show maximum values at Al/Ni = 1.0.

A similar concept can be applied to explain the compositional dependence of $T_s$ in the Al-rich amorphous alloys. The Al-rich amorphous phase is formed in the vicinity of Al$_{10}$Ni$_{10}$Zr$_{10}$ $^{10}$. The $T_m$ of Al-Zr and Al-Ni binary alloys decreases significantly from 1853 to 933 K and from 1373 to 913 K, respectively, with decreasing Zr or Ni content from 25 to 0%. The compositional effect on $T_s$ for the Al-rich amorphous alloys is similar to that for $T_m$. Accordingly, the decrease of $T_s$ for the Zr-Al-Ni amorphous alloys with a further increase of Al content from about 60 to 80 at% seems to result from the short-range atomic configuration which reflects the change of the equilibrium phases leading to the decrease in $T_m$. Clarification of the short-range atomic configuration to confirm the above-described concept is in progress for the Zr-Al-Ni amorphous alloys.

2. Compositional effect on $\Delta T_s$, $T_s/T_m$ and $\Delta H_s$

As shown in Fig. 4, the supercooled liquid region at temperatures below $T_s$ was observed over the wide compositional range for the Zr-Al-Ni amorphous alloys. It is
particularly notable that the temperature span ($\Delta T_s$) of the supercooled liquid is as large as 75 K in the vicinity of 20%Al and 20%Ni. Furthermore, it was shown in section III that the amorphous alloys with the large $\Delta T_s$ values had high $T_s/T_m$ values reaching about 0.64. The large values of $\Delta T_s$ and $T_s/T_m$ indicate that the supercooled liquid of the Zr–Al–Ni amorphous alloys has a high stability to the nucleation and growth of crystalline phases. In other words, the retardation of the transformation to a crystalline phase for the supercooled liquid is thought to bring about the high values of $\Delta T_s$ and $T_s/T_m$. The reason why the large values of $\Delta T_s$ and $T_s/T_m$ are obtained in the vicinity of Zr$_{60}$Al$_{20}$Ni$_{20}$ is discussed in this section. The equilibrium phase diagrams of Zr–Al($^{(9)}$) and Zr–Ni($^{(9)}$) binary alloys show the existence of a deep trough in the range of 70 to 75 %Zr, indicating a high stability of the liquidus structure at their alloy compositions. The ratios of Al and Ni to Zr at the compositions are nearly equal to those for the Zr$_{60}$Al$_{20}$Ni$_{20}$ alloy with the large $\Delta T_s$ and $T_s/T_m$ values. The agreement suggests that the liquidus structure is more stable in the vicinity of Zr$_{60}$Al$_{20}$Ni$_{20}$. The existence of the deep trough suggests an ease of obtaining a supercooled state probably because of the high stability of the supercooled liquid near the composition. Thus, the equilibrium phase diagrams allow us to presume that the high stability of the supercooled liquid is closely related to an ease of supercooling of the liquid state. Although one can remind of a number of eutectic-type alloy systems having an easy supercooling capacity of liquid, no amorphous alloys with the large $\Delta T_s$ have been obtained in most of the eutectic-type alloys($^{(11)}$). A similar large $\Delta T_s$ value in the eutectic-type system has recently been obtained in La$_{10}$Al$_{51}$Ni$_{39}$($^{(12)}$) and La$_{10}$Al$_{25}$Cu$_{65}$($^{(13)}$) alloys. The exceptionally high stability of the supercooled liquid in the Zr$_3$Al–Ni alloy as well as in the La$_{10}$Al$_{51}$Ni$_{39}$ and La$_{10}$Al$_{25}$Cu$_{65}$ alloys seems to be attributed to the unique bonding and packing states of the Zr–Al–Ni and La–Al–Ni or Cu amorphous alloys with the stoichiometric compositions. The electronic structure and bonding nature of the Zr–Al–Ni amorphous alloys are also under investigation.

It is shown in Fig. 5 that the $\Delta H_s$ also tends to have a maximum value in the vicinity of Zr$_{60}$Al$_{20}$Ni$_{20}$. It is generally known that the $\Delta H_s$ reflects a change of internal energy, since the contribution of external pressure may be neglected. It has crudely been said that the change of internal energy is related to the integral of the atomic forces over the interatomic distance change in collapse from the amorphous to the crystalline phase. Accordingly, a larger $\Delta H_s$ is expected when the constituent atoms in the amorphous phase are densely packed in a tightly bonding state. From the appearance of the maximum $\Delta H_s$ value in the vicinity of Zr$_3$Al$_2$Ni$_3$, it is presumed that the amorphous alloys near the stoichiometric composition have a more dense atomic configuration and/or a stronger bonding force which are caused by an optimization of atomic size and electronic bonding state. The amorphous structure with dense atomic configuration and strong bonding force is thought to result in an increase of the difficulty in the diffusivity of constituent atoms, leading to the increase of the stability of the supercooled liquid, i.e., the increase of $\Delta T_s$ and $T_s/T_m$.

3. Glass-forming capacity

As described above, the large $\Delta T_s$ values imply that the supercooled liquid can exist in a wide temperature range without crystallization and has a high resistance to the nucleation and growth of crystalline phases. The high resistance also implies that the supercooled liquid obtained by melt spinning can also have a high resistance to the nucleation and growth of crystalline phases, leading to a high glass-forming capacity. It is known that the $T_s/T_m$ value is closely related to the glass-forming capacity and the higher the $T_s/T_m$ value the larger is the glass-forming capacity. The empirical relation($^{(14)}$) between $T_s/T_m$ and the minimum cooling rate for the formation of an amorphous phase allows us to evaluate that the minimum cooling rate for the Zr$_{60}$Al$_{20}$Ni$_{20}$ alloy is as small as about 10$^3$ K/s. The cooling rate is almost comparable to that which can be achieved by water quenching, suggesting the possibility of obtaining an amorphous bulk by water quenching. The possibility has been confirmed by an evidence($^{(15)}$) that an amorphous Zr$_{60}$Al$_{20}$Ni$_{20}$ alloy with a cylindrical form in the diameter range below 1.4 mm is formed by water quenching.

The high $T_s/T_m$ value also implies that the viscosity of the supercooled liquid can reach about 10$^{12}$ Pa.s by a lower degree of supercooling. It is thus said that the temperature dependence of viscosity of the supercooled liquid is very steep. The steep increase of viscosity with decreasing temperature is presumably due to a rapid increase in the difficulty of the diffusivity of the constituent atoms. As described in section IV-3, the difficulty of the diffusivity is thought to take place by the achievement of a tightly bonding and densely packed states of the constituent atoms. Considering that the alloys exhibiting the largest values of $\Delta T_s$ and $T_s/T_m$ are located in the vicinity of Zr$_{60}$Al$_{20}$Ni$_{20}$ (Zr$_3$Al$_2$Ni$_3$), the short-range atomic configuration which reflects the stoichiometric Zr$_3$Al$_2$Ni$_3$ compound may be favorable for the suppression of the diffusivity of the constituent atoms. Research of the atomic configuration in the Zr$_3$Al$_2$Ni$_3$ amorphous alloy with the stoichiometric composition is expected to shed main light on the clarification of the mechanism for the large values of $\Delta T_s$, $T_s/T_m$ and $\Delta H_s$ as well as the large glass-forming capacity.

4. The reason for the effectiveness of Al addition

It has been reported($^{(16)}$) that the glass transition is scarcely observed in Zr-rich Zr–Ni binary amorphous alloys and the $\Delta T_s$ is below 10 K. Accordingly, it is interpreted that the dissolution of Al into the Zr-rich Zr–Ni amorphous alloys results in a distinct appearance of the glass transition through an increase of thermal stability of the supercooled liquid. In addition, it was shown in section III that all the properties of $T_s$, $T_m$, $\Delta H_s$, $H$, and $\sigma_i$ increase significantly by the dissolution of an optimum amount of Al, in comparison with those for the Zr-rich
Zr–Ni amorphous alloys. The reason why the thermal stability of the supercooled liquid and the properties of the amorphous solid increase by the dissolution of Al is discussed in this section. It was presumed in section IV-1 that the atomic configuration on a short-range scale reflects the equilibrium intermetallic compounds. This concept originates mainly from the change in the chemical (or compositional) short-range ordering in the Zr-rich Zr–Ni amorphous alloys by the dissolution of Al. As another concept to discuss the thermal stability in the amorphous phase, one can remind of a topological short-range ordering. It is generally believed that the higher the packing density the higher are the thermal stability and mechanical strength of an amorphous phase (or the higher is the resistance of the supercooled liquid against the transformation into crystalline phases). The atomic radius of Zr, Al and Ni is 0.160, 0.143 and 0.124 nm, respectively, and hence the size of Al is located between Zr and Ni. The intermediate atomic size of Al is presumed to be appropriate to fill up the vacant site in the disordered structure consisting of Zr and Ni with a large difference in atomic size, leading to an increase of the packing density in the amorphous solid and supercooled liquid. It is therefore presumed that the high stability of the supercooled liquid and the improved properties of the amorphous solid originate partly from the increase of the packing fraction in the amorphous structure by the dissolution of Al. In other words, the low thermal stability and mechanical strengths of Zr-rich Zr–Ni binary amorphous alloys are probably because the amorphous structure has a more loose atomic configuration as compared with that for the Zr–Ni–Al ternary amorphous alloys. This concept is supported from the previous and present results; the alloy systems in which the addition of Al brings about a significant increase of the $\Delta T_c$ and $T_e/T_m$ as well as the $T_p$, $T_c$, $\Delta H_c$, $H_c$ and $\sigma_T$ are always composed of the elements with the atomic sizes which are considerably larger or smaller than that of Al, as exemplified for Zr–Al–Ni and La–Al–Ni or Cu–Al alloys, in addition to a large negative enthalpy of mixing between Al and Zr or Ni.

V. Summary

In order to find amorphous alloys exhibiting a wide supercooled liquid region, a high glass-forming capacity and high mechanical strengths in alloy systems without noble and lanthanide metals by liquid quenching, the rapidly solidified structure in Zr–Al–Ni ternary system was examined over a wide compositional range. The amorphous alloys are formed in a wide compositional range which extends from 0 to 37% Al and 3 to 67% Ni, in addition to a narrow composition range of 3 to 17% Zr and 7 to 33% Ni for the Al-rich alloys. Furthermore, the Zr–Al–Ni amorphous alloys exhibit a supercooled liquid region in a wide glass formation range at the Zr-rich composition side. In particular, the alloy which is located in the vicinity of Zr$_{50}$Al$_{20}$Ni$_{30}$ has a large temperature span $\Delta T_c = (T_c - T_p)$ exceeding 70 K and a high $T_e/T_m$ value above 0.6. The $\Delta T_c$ value is believed to be the largest in metallic amorphous materials. The large values of $\Delta T_c$ and $T_e/T_m$ indicate that the supercooled liquid has the high stability of the transformation to a crystalline phase and the viscosity increases steeply with increasing the degree of supercooling. The high stability of the supercooled liquid and the steep increase of viscosity are explained by the presumption that the amorphous structure is in optimally bonding and packing states at the stoichiometric composition of Zr$_{50}$Al$_{20}$Ni$_{30}$. The $T_c$ and $H_c$ of the Zr-rich amorphous alloys increase from 660 to 860 K and 400 to 720 with increasing Al and Ni contents and the increase is more remarkable for the alloys containing an equivalent concentration of Al and Ni. The $E$ and $\sigma_T$ values also show a similar compositional effect and the highest $\sigma_T$ value is about 1720 MPa for Zr$_{50}$Al$_{20}$Ni$_{30}$ alloy. The compositional effect on $T_e$, $H_c$, $E$ and $\sigma_T$ is presumed to result from the change in the short-range atomic configuration which reflects the change of the equilibrium compounds because of the similarities in the compositional dependence of $T_m$.

REFERENCES