

Amorphous Zr-Al-TM (TM=Co, Ni, Cu) Alloys with Significant Supercooled Liquid Region of Over 100 K

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Amorphous alloys exhibiting a wide supercooled liquid region above 100 K were found to form in a compositional range from 0 to 3%Co, 0 to 15%Ni and 10 to 23%Cu in $\text{Zr}_{65}\text{Al}_{17.5}\text{Cu}_{2.5}(\text{Co}_{1-x-y}\text{Ni}_x\text{Cu}_y)_{25}$ system by melt spinning. The temperature span $\Delta T_x (= T_x - T_g)$ between glass transition temperature (T_g) and crystallization temperature (T_x) reaches as large as 127 K for $\text{Zr}_{65}\text{Al}_{17.5}\text{Ni}_{10}\text{Cu}_{17.5}$. The T_g and hardness (H_v) increase from 622 to 685 K and 426 to 502 with increasing Co content while the T_x decreases from 749 to 690 K, resulting in the decrease of ΔT_x from 127 to 30 K with increasing Co content. The compositional effect on T_g , T_x , ΔT_x and H_v indicates that there is no close relation between the magnitude of the attractive bonding force and the stability of the supercooled liquid. The high stability of the supercooled liquid against the nucleation and growth of a crystalline phase in the limited composition range seems to result from a highly dense random packing structure consisting of atoms with an optimum atomic size ratio and a large negative enthalpy of mixing.

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I. Introduction

The existence of a wide supercooled liquid region at temperatures below the onset temperature of crystallization is expected to result in the warm-working to various bulk shapes through a large viscous flowability of the supercooled liquid. In addition, the production of an amorphous bulk by casting the melt into a metallic mold seems to be possible through the high resistance of the supercooled liquid against the nucleation and growth of a crystalline phase. Accordingly, search into an amorphous metallic system exhibiting a significant supercooled liquid region before crystallization comparable to that for glassy oxides and fluorides is important in a subsequent progress of amorphous metallic materials. It has previously been reported⁽¹⁾ that the formation of an amorphous alloy with significant supercooled liquid region is limited to noble metal base systems such as Pd-Ni-P, Pd-Ni-Si and Pt-Ni-P etc. More recently, the present authors have reported that a similar wide supercooled liquid region appears in new metal-metal type amorphous systems such as La-Al-Ni⁽²⁾, La-Al-Cu⁽³⁾, Zr-Al-Ni⁽⁴⁾ and Mg-Ni-Y⁽⁵⁾, etc. The largest temperature span between T_g and T_x , $\Delta T_x (= T_x - T_g)$ in these metal-metal type amorphous alloys reaches as large as 71 K. In a subsequent study on the search of an amorphous alloy with a larger ΔT_x value, we have found that an extremely wide supercooled liquid region above 100 K appears in the temperature range below T_x for amorphous alloys in

the Zr-Al-TM (TM=Co, Ni, Cu) quaternary and pentad systems. The first aim of this paper is to clarify the alloy composition of the Zr-Al-TM amorphous alloys exhibiting the wide supercooled liquid region and the sequent transformation behavior of amorphous solid, glass transition, supercooled liquid and crystalline solid for the amorphous alloys with large ΔT_x values above 100 K. The second is to investigate the reason for the appearance of the extremely wide supercooled liquid region in the Zr-Al-TM amorphous alloys.

II. Experimental Procedure

Quaternary and pentad alloys in Zr-Al-TM (TM=Co, Ni, Cu) system were used in the present study. Their ingots were prepared by arc-melting a mixture of pure Zr (99.6 mass%), Al (99.99 mass%), Co (99.5 mass%), Ni (99.9 mass%) and Cu (99.99 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 $0.03 \times 1.5 \text{ mm}^2$ were prepared by a single roller melt-spinning technique in an argon atmosphere. The amorphicity of the melt-spun ribbons was examined by X-ray diffractometry and transmission electron microscopy techniques. The specific heat (C_p) associated with the sequent structural change in amorphous solid, glass transition, supercooled liquid and crystallization was measured with a differential scanning calorimeter (DSC). The accuracy of the data was about $\pm 0.4 \text{ J/mol}\cdot\text{K}$ for absolute C_p values and better than $\pm 0.1 \text{ J/mol}\cdot\text{K}$ for the relative C_p or ΔC_p measurements. The samples were first scanned at 0.67 K/s (40 K/min) to the temperature of the supercooled liquid to obtain data in the as-quenched state, and

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then cooled to room temperature. The $C_p(T)$ measurement was immediately repeated *in situ* to obtain the 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 of the ribbon specimens was measured by a Vickers microhardness tester with a 0.98 N (100 gf load). Eight to ten symmetrical indentations were used to determine the average microhardness value.

III. Results

Figure 1 shows the composition range in which an amorphous phase in $Zr_{65}Al_{7.5}Cu_{2.5}(Co_{1-x-y}Ni_xCu_y)_{25}$ alloys is formed by melt spinning, along with the data of bending ductility of the amorphous alloys. The alloy composition of $Zr_{65}Al_{7.5}TM_{27.5}$ was chosen because the largest ΔT_x value was obtained in $Zr_{65}Al_{7.5}Cu_{27.5}$. An amorphous phase was formed over the entire composition range and all the amorphous alloys were found to exhibit good bending ductility which is shown by a 180 degree bending without fracture. Figure 2 shows the compositional dependence of T_x for the $Zr_{65}Al_{7.5}Cu_{2.5}(Co, Ni, Cu)_{25}$ amorphous alloys. As is evident from the contour lines, the T_x value shows a minimum around $Zr_{65}Al_{7.5}Cu_{2.5}Co_{10}Ni_{15}$ and increases gradually with a deviation from the composition. Particularly, the increase in T_x with increasing Cu content is significant. The highest T_x is 750 K in the vicinity of $Zr_{65}Al_{7.5}Ni_5Cu_{22.5}$. Considering that the melting and boiling temperatures of the TM elements are the highest for Co, followed by Ni and then Cu, the compositional effect on T_x for the Zr-Al-Co-Ni-Cu amorphous alloys is independent of the bonding nature of the TM elements themselves. The in-

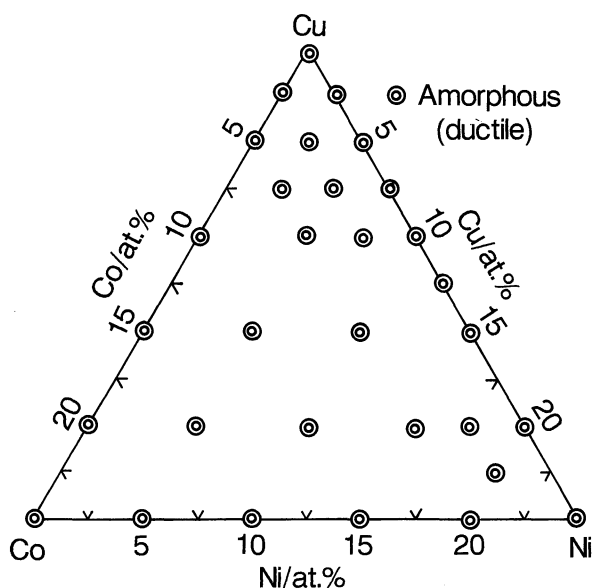


Fig. 1 Composition range for formation of the amorphous phase in the $Zr_{65}Al_{7.5}Cu_{2.5}(Co_{1-x-y}Ni_xCu_y)_{25}$ system. The symbol marked with a double open circle represents the formation of an amorphous phase with good bending ductility.

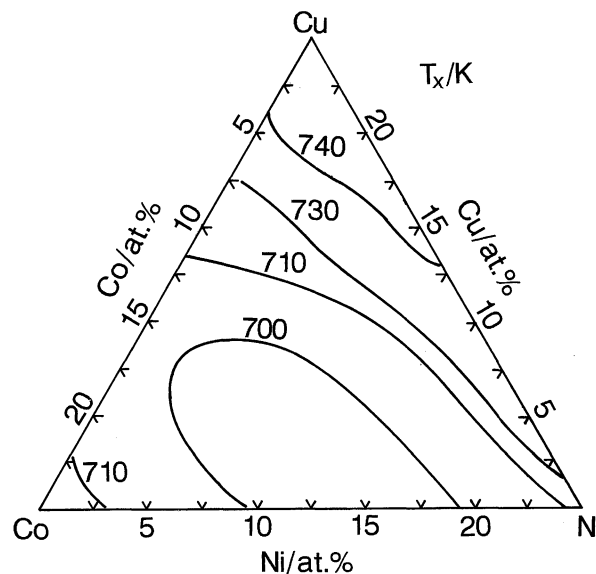


Fig. 2 Compositional dependence of the onset temperature of crystallization (T_x) of $Zr_{65}Al_{7.5}Cu_{2.5}(Co_{1-x-y}Ni_xCu_y)_{25}$ amorphous alloys.

dependence suggests that the thermal stability of the Zr-Al-Co-Ni-Cu amorphous alloys is dominated by the bonding nature among the different atoms.

As examples, Fig. 3 shows the DSC curves of $Zr_{65}Al_{7.5}Ni_5Cu_{22.5}$, $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{65}Al_{7.5}Ni_{15}Cu_{12.5}$ amorphous alloys exhibiting higher T_x values. It is seen that the three alloys crystallize through a single stage accompanied by an exothermic heat ranging from 3.13 to 3.74 kJ/mol. In addition to the exothermic peak, one can notice an endothermic reaction with very wide temperature span in the temperature range below the onset temperature of crystallization (T_x). For instance, the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ amorphous alloy begins to transform from the amorphous solid to a supercooled liquid at about 630 K and keeps the supercooled liquid state in a wide temperature span reaching 120 K, followed by crystallization at about 750 K. The largest temperature span of the supercooled liquid region for amorphous metallic materials is known to be 50 to 70 K for Pt-Ni-P⁽⁶⁾, Pd-Ni-P⁽⁶⁾, La-Al-Ni⁽²⁾, Zr-Al-Ni⁽⁴⁾, Mg-Ni-La⁽⁷⁾, etc. It is therefore said that the largest ΔT_x value of the Zr-Al-Ni-Cu alloys is about 1.5 times as large as the largest value in all amorphous alloys reported up to date.

Figure 4 shows the compositional dependence of T_g for $Zr_{65}Al_{7.5}Cu_{2.5}(Co, Ni, Cu)_{25}$ amorphous alloys. The T_g value shows the lowest value of 622 K for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and increases to 685 K with increasing Co and Ni contents. In comparison with the data of T_x shown in Fig. 2, one can notice that the compositional dependence of T_g is roughly inverse to that of T_x . That is, there is a tendency for T_g to increase with an increase of the melting temperature of the TM elements. Based on the data shown in Figs. 2 and 4, the compositional effect on the ΔT_x value for the $Zr_{65}Al_{7.5}Cu_{2.5}TM_{25}$ amorphous alloys is shown in Fig. 5. The ΔT_x value is maximum (127 K) for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and decreases with a devia-

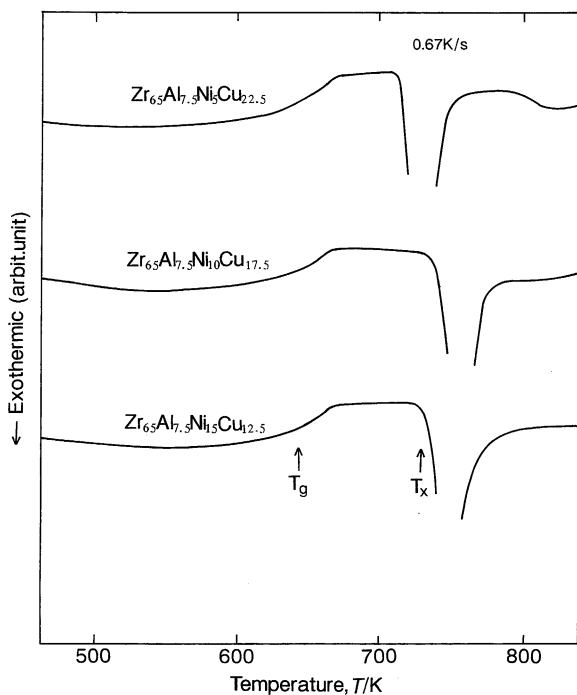


Fig. 3 Differential scanning calorimetric (DSC) curves of amorphous $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_5\text{Cu}_{22.5}$, $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{15}\text{Cu}_{12.5}$ alloys.

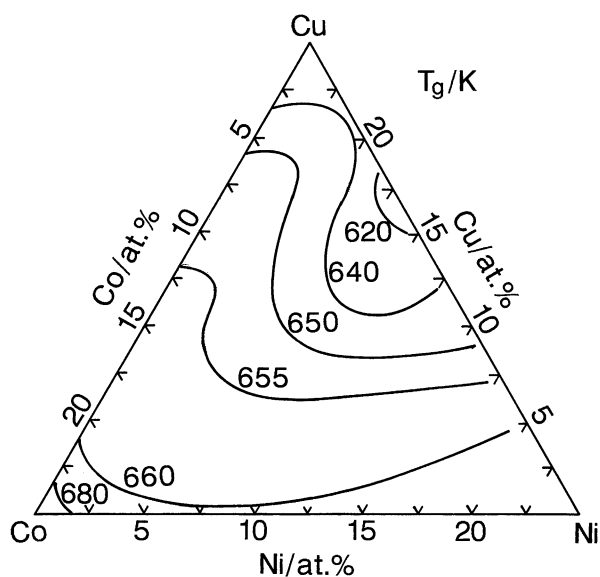


Fig. 4 Compositional dependence of the glass transition temperature (T_g) of $\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{2.5}(\text{Co}_{1-x-y}\text{Ni}_x\text{Cu}_y)_{25}$ amorphous alloys.

tion from the alloy component. The decrease of the ΔT_x is more significant with increasing Co content, though all the Zr–Al–Co–Ni–Cu amorphous alloys exhibit a supercooled liquid region above 30 K. The compositional dependence of the ΔT_x value is similar to that of T_x and the higher thermal stability is obtained in a simultaneous dissolution of Cu and Ni elements. Thus, the thermal stability of the supercooled liquid against the nucleation and growth of a crystalline phase is independent of the melting and boiling temperatures of the TM elements and

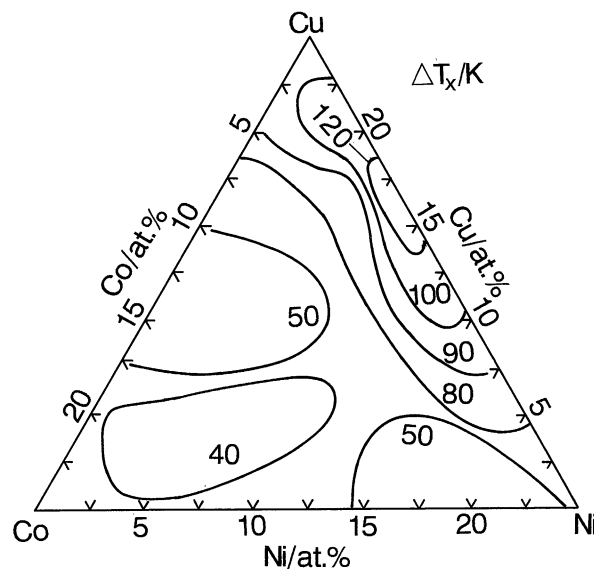


Fig. 5 Compositional dependence of the temperature span ΔT_x between T_g and T_x of $\text{Zr}_{65}\text{Al}_{7.5}\text{Cu}_{2.5}(\text{Co}_{1-x-y}\text{Ni}_x\text{Cu}_y)_{25}$ amorphous alloys.

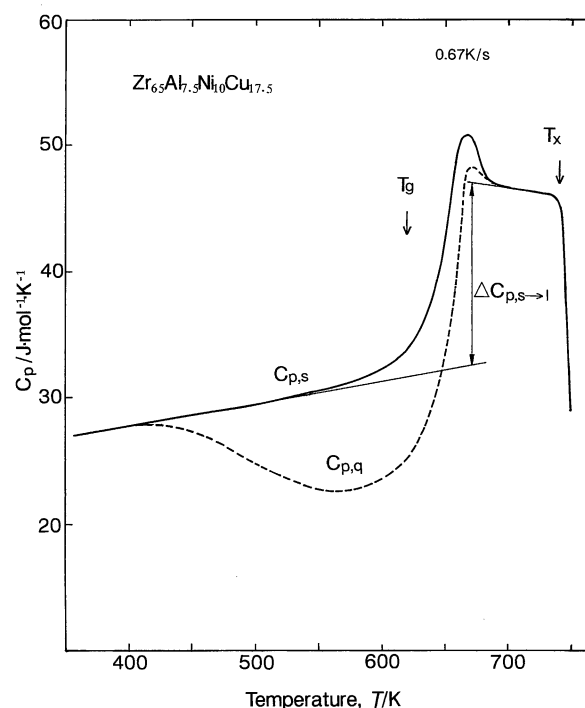


Fig. 6 The thermogram $C_{p,q}(T)$ of an amorphous $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy in the as-quenched state. The solid line represents the thermogram $C_{p,s}(T)$ of the sample heated to 720 K.

decreases significantly with increasing Co content.

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–Cu amorphous alloys with large ΔT_x values above 100 K. Figure 6 shows the thermograms of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ amorphous alloy with the

largest ΔT_x value of 127 K. The C_p value of the as-quenched phase is 26.9 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 410 K. With a further increase in temperature, the C_p value shows its minimum at about 570 K, then increases rapidly in the glass transition range from 600 to 670 K and reaches 47.0 J/mol·K for the supercooled liquid around 685 K. With further increased temperature, the C_p value of the supercooled liquid decreases gradually and then rapidly due to crystallization at 740 K. It is seen in Fig. 6 that the transition of the amorphous solid to the supercooled liquid takes place accompanied by a large increase in the specific heat, $\Delta C_{p,s \rightarrow l}$, reaching 14.5 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 $\Delta C_{p,s \rightarrow l}$ value for the $Zr_{65}Al_{7.5}Cu_{2.5}TM_{25}$ amorphous alloys was examined as a function of TM composition. As a result, it was found that the $\Delta C_{p,s \rightarrow l}$ value is in the range of 13 to 15 J/mol·K over the whole composition range and no distinct compositional dependence of the $\Delta C_{p,s \rightarrow l}$ value is seen for the Zr–Al–Cu–TM alloys with ΔT_x values larger than about 30 K.

It is important to examine the reduced glass transition temperature (T_g/T_m) for the Zr–Al–Cu–TM amorphous alloys exhibiting the wide supercooled liquid region. As an example, Fig. 7 shows the DTA curves during heating and cooling at 0.33 K/s for a $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ amorphous alloy with the largest ΔT_x value. It is seen that the fusion phenomenon appears through an endothermic reaction on the heating curve in the temperature range above T_x and an exothermic reaction on the cooling curve. When the onset temperature of the endothermic or the exothermic reaction is regarded as a melting temperature (T_m), the T_g/T_m value can be evaluated to be 0.58 for the Zr–Al–Ni–Cu alloy. Similarly, the T_g/T_m value was measured to be 0.58 for $Zr_{65}Al_{7.5}Ni_{12.5}Cu_{15}$ and 0.59 for $Zr_{65}Al_{7.5}Co_5Ni_5Cu_{17.5}$. Unexpectedly, no amorphous alloy exhibiting T_g/T_m values above 0.60 is obtained in the Zr–Al–TM system. The T_g/T_m value is nearly the same as that (0.57 to 0.59) for Al–Ln–TM (Ln=lanthanide metal) amorphous alloys in which the ΔT_x value is as small as 20 to 30 K⁽⁸⁾. These results indicate that there is no close relation between ΔT_x and T_g/T_m . We have confirmed⁽⁹⁾ that the Zr–Al–Ni–Cu alloys can be amorphized in a cylindrical form by the metallic mold casting method. The critical diameter for formation of an amorphous phase is as large as about 7.0 mm for the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ with the largest ΔT_x and decreases to about 1.5 mm with a decrease of ΔT_x to 40 K, though the T_g/T_m value is almost independent of TM composition. Accordingly, a unique amorphous structure leading to

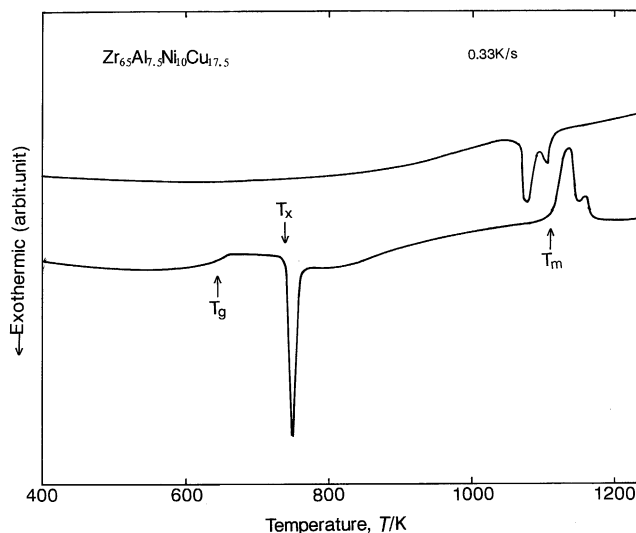


Fig. 7 Differential thermal analytical (DTA) curves of a $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ amorphous alloy.

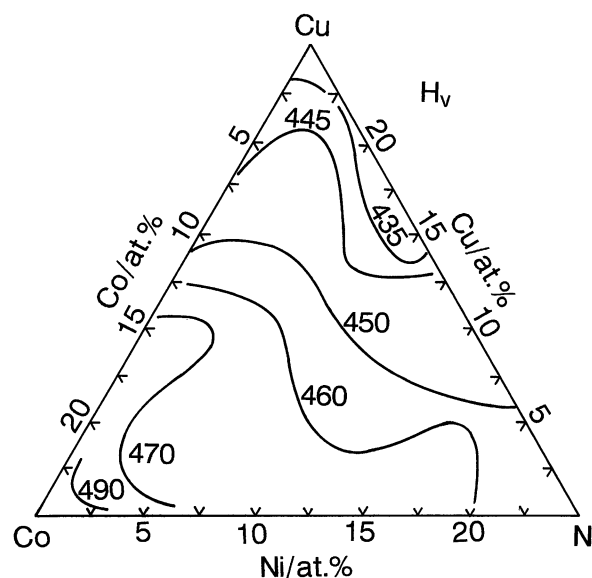


Fig. 8 Compositional dependence of Vickers hardness number (H_v) of $Zr_{65}Al_{7.5}Cu_{2.5}(Co_{1-x-y}Ni_xCu_y)_{25}$ alloys.

the large ΔT_x value is thought to be the origin for the high glass-forming capacity of the Zr–Al–TM alloys.

Vickers hardness (H_v) was measured for the $Zr_{65}Al_{7.5}Cu_{2.5}TM_{25}$ amorphous alloys with the aim of evaluating the compositional effect on the magnitude of bonding force of the constituent elements. As shown in Fig. 8, the H_v number is 435 in the vicinity of $Zr_{65}Al_{7.5}Ni_{17.5}Cu_{20}$, increases gradually with increasing Co and Ni contents. The compositional effect on the bonding nature is dependent on the melting and boiling temperatures of the TM elements themselves. The feature of the compositional effect on H_v is analogous to that for T_g and is inverse to that for ΔT_x . These compositional dependences suggest that the bonding force of the amorphous solid represented by T_g and H_v is dominated

by the bonding nature among the different constituent elements while the thermal stability of the supercooled liquid represented by T_x and ΔT_x is independent of the bonding nature of the TM elements themselves and among the different constituent elements. That is, the ease of nucleation and growth of a crystalline phase is independent of the bonding nature among the constituent elements and seems to be dominated by other factors.

IV. Discussion

It has been reported⁽¹⁰⁾ that the glass transition is scarcely observed in Zr-rich Zr-Ni and Zr-Cu binary and Zr-Ni-Cu ternary amorphous alloys and the ΔT_x is below 10 K for the binary and ternary alloys. In addition, no glass transition is observed in Zr-rich Zr-Co amorphous alloys⁽¹¹⁾. Accordingly, it is interpreted that the dissolution of Al into the Zr-rich Zr-TM binary and ternary amorphous alloys results in a distinct appearance of the glass transition through an increase of thermal stability of the supercooled liquid. Furthermore, it has previously been shown⁽⁴⁾ that the T_x , ΔT_x and hardness (H_v) of Zr-Ni-Al and Zr-Cu-Al amorphous alloys increase significantly by the dissolution of an optimum amount of Al, in comparison with those for the Zr-rich Zr-TM binary amorphous alloys. Here, we shall discuss the reason why the thermal stability of the supercooled liquid (ΔT_x) in the Zr-rich Zr-TM system and the T_x and H_v of the Zr-rich Zr-TM amorphous solid increase by the dissolution of Al. It has previously been pointed out⁽¹²⁾ that the atomic configuration on a short-range scale reflects the corresponding equilibrium intermetallic compounds. This concept originates mainly from the change in the chemical (or compositional) short-range ordering in the Zr-rich Zr-TM 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, Co, Ni and Cu is 0.160, 0.143, 0.125, 0.125 and 0.128 nm, respectively, and hence the size of Al is located between Zr and TM. 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 TM with large differences 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 lower thermal stability and the lower hardness of Zr-rich Zr-TM amorphous alloys are probably because the amorphous structure has a more loose atomic configuration as compared with those for the Zr-Al-TM amorphous alloys. Furthermore, the coexistence

of Cu and Co or Ni is thought to cause a further increase of the packing fraction in the disordered structure presumably because of the slight difference in atomic size between Cu and Co or Ni as well as in the bonding nature of Cu and Co or Ni against the other constituent elements. Similarly, the reason why no significant increase of ΔT_x is seen by the addition of Co to the Zr-Al-Ni-Cu alloys is presumably due to the same atomic size of Co and Ni elements. 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 ΔT_x are always composed of the elements with the atomic sizes which are considerably larger or smaller than that of Al, in addition to a large negative enthalpy of mixing between Al and Zr or TM, as exemplified for Zr-Al-(Co, Ni, Cu), Ln-Al-(Ni or Cu)⁽²⁾⁽³⁾ and Mg-Ln-(Ni or Cu)⁽⁵⁾⁽⁷⁾ alloys. In addition, the formation of a more dense random packing structure in their amorphous alloys consisting of three different elements with larger, intermediate and smaller atomic sizes has been confirmed in the structure data⁽¹²⁾ of Mg-Ln-(Ni or Cu) amorphous alloys⁽¹³⁾ obtained by the anomalous X-ray diffractometry technique.

V. Summary

Amorphous alloys exhibiting a wide supercooled liquid region were searched in the $Zr_{65}Al_{7.5}Cu_{2.5}(Co_{1-x-y}Ni_xCu_y)_{25}$ system. The amorphous alloys exhibiting good bending ductility are formed in the entire composition range. Furthermore, all the Zr-Al-TM (TM=Co, Ni, Cu) amorphous alloys exhibit a supercooled liquid region with the large temperature span above about 30 K. In particular, the alloy in the vicinity of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ has the largest temperature span $\Delta T_x (= T_x - T_g)$ reaching 127 K. The ΔT_x value is believed to be the largest in metallic amorphous materials reported up to date. The T_g and H_v of the Zr-Al-TM amorphous alloys increase from 622 to 685 K and 426 to 502 with increasing Co content while the T_x has an inverse compositional dependence and decreases from 749 to 690 K. The compositional effect on T_g , T_x , ΔT_x and H_v indicates an absence of a close relation between the magnitude of the bonding nature among the constituent elements and the thermal stability of the supercooled liquid. The extremely high stability of the supercooled liquid against crystallization is presumably because the multiplication to the quaternary and pentad systems results in the formation of a more dense random packing structure through an optimization of atomic size ratio.

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