Thermal Stability of Zr-Based Glassy Alloys Examined by Electrical Resistance Measurement

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The effects of the thermal histories during the sample preparation and in measuring the physical properties on thermal stabilities of glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ and $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloys were examined mainly by the electrical resistance measurement. As long as the present experiments are concerned, the glass transition and crystallization temperature were not significantly affected by the thermal histories as for as-quenched samples. The temperature derivative of the electrical resistance dR/dT exhibited a negative value below the glass transition temperature. In the contrast, dR/dT was turned to a positive value in the supercooled liquid region. Although dR/dT showed an almost constant value for glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy, an apparent two step change was observed for glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloy in the supercooled liquid region. It was found out that the dR/dT in the supercooled liquid region was significantly affected by the thermal history, especially the atmosphere in measuring the electrical resistance. Even for the sample where the oxide layer of the surface was taken away by mechanical polishing and the resistance measurement was carried out in the vacuum, the dR/dT retained a small positive value in the supercooled liquid region.

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I. Introduction

Since the glassy alloys with a significant supercooled liquid region have been discovered by A. Inoue *et al.*⁽¹⁾⁻⁽⁴⁾, many studies on the compositional dependence of amorphous formation range⁽¹⁾⁻⁽⁴⁾, the characteristic amorphous structure⁽⁵⁾, the mechanical properties⁽⁶⁾, the glass transition and/or the structural relaxation⁽⁷⁾, the crystallization process⁽⁸⁾⁽⁹⁾ and so on have been carried out extensively. It has been reported⁽⁴⁾ that Zr-based glassy alloys exhibit the easy amorphous formation ability and the high resistance to crystallization. Also it has been reported⁽⁶⁾ that the $\Delta T_x = T_x - T_g$, where T_x and T_g are the crystallization and glass transition temperatures, respectively, reaches to about 116 K for a very stable $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloy. The origin of these interesting properties can be interpreted by an atomic size effect and a characteristic bonding state between atoms⁽⁴⁾⁽⁹⁾. However, little is reported about the basic properties for Zr-based glassy alloys such as the effects of the thermal history on the stabilities of these alloy systems. It is important scientifically and technologically to investigate in detail the thermal stabilities for these alloy systems. In the present experiments, the stabilities of typical glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ and $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloys undergoing the different thermal histories will be examined. One of the thermal history is the quenching condition and the other is the gas atmosphere used in measuring the physical properties. The quenching condition may give an influence on the density and the size distribution of the quenched-in nucleus. Since it has been reported⁽¹⁰⁾⁽¹¹⁾ that

the oxide layer is easy to be formed in the surface of the Zr-based amorphous alloy, it may be important to control the amount of oxygen impurity in the atmosphere used in measuring the physical properties.

II. Experimental Procedures

The alloys with the composition of $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ and $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ in at.% were prepared by arc-melting. The amorphous ribbons were produced by an usual melt-spinning technique with a single copper roller. To change the quenching rate and the surface state of the sample, the surface velocity v_s of rotating roller was varied from about 20 to 40 m/s and the quenching operation was carried out in the atmosphere of purified Ar (99.9995%) and vacuum (1.0×10^{-4} Torr) for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy. On the other hand, for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloy, the amorphous ribbon was prepared with the surface velocity of $v_s = 40$ m/s in the Ar atmosphere only. The amorphicity of sample was checked by X-ray diffraction, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The thermal stability of sample was investigated mainly by electrical resistance measurement with usual four terminal d.c. method. Of course, some DSC measurements were simultaneously performed under the same experimental conditions (the heating rate and the atmosphere in measuring) as the electrical resistance measurement, to compare with the glass transition and the crystallization behaviors. The heating rate of 0.67 K/s was used commonly through electrical resistance and DSC measurements. The dynamical heating in electrical resistance measurement was carried out

by means of the infrared image furnace coupled with the thermal controller. The atmosphere in measuring the electrical resistance was changed to purified Ar (99.9995%), He (99.9999%) and vacuum (5.0×10^{-6} Torr) to examine the influence of the surface oxidation of the sample during annealing on the thermal stability. Auger electron spectroscopy was employed to investigate the nominal composition of sample as a function of the depth from the surface of the sample.

III. Results

Figure 1 shows the X-ray diffraction profiles measured with a Cu- $K\alpha$ radiation respectively for glassy $Zr_{60}Al_{15}Ni_{25}$ and $Zr_{60}Al_{15}Ni_{7.5}Co_{2.5}Cu_{15}$ alloys which were prepared with $v_s=40$ m/s in an Ar atmosphere. Any traces of crystallite are invisible in the profiles. The DSC thermogram and the corresponding electrical resistance curve, $R(T)/R_0$, around the supercooled liquid region are shown comparatively in Fig. 2 for the $Zr_{60}Al_{15}Ni_{25}$ alloy, where R_0 and $R(T)$ represent the electrical resistance at 300 K and the temperature T , and the both measurements were carried out in the Ar atmosphere. The temperature derivative curve is also plotted in this figure, because the onset of the glass transition is not obvious on the electrical resistance curve in this case. The glass transition temperature T_g determined from the differential curve agrees acceptably with T_g on the DSC thermogram. The crystallization temperature T_x also agrees well with each other. Since it is confirmed that T_g and T_x estimated from the electrical resistance measurement are in good agreement with those of DSC thermogram, the electrical resistance measurement was only used to investigate the thermal stability of glassy alloys. The typical change in the electrical resistance with increasing annealing temperature was shown in Fig. 3 for $Zr_{60}Al_{15}Ni_{25}$. The electrical resistance around the room temperature decreases with increasing temperature. It has been reported⁽¹²⁾ that an amorphous $(Ni_{33}Zr_{67})_{0.85}Al_{0.15}$ alloy exhibits a negative temperature derivative of the resistivity in the temperature range from 3 to 300 K. Before the glass transition occurs, the electrical resistance increases temporary, starting from about 450 K, although the temperature deriva-

Fig. 1 X-ray diffraction profiles respectively for glassy $Zr_{60}Al_{15}Ni_{25}$ and $Zr_{60}Al_{15}Ni_{7.5}Co_{2.5}Cu_{15}$ alloys measured with Cu- $K\alpha$ radiation.

Fig. 2 DSC thermogram and electrical resistance curve along with its temperature derivative curve around the supercooled liquid region. The samples were prepared with $v_s=40$ m/s in Ar atmosphere. All measurements were carried out in Ar atmosphere.

Fig. 3 Change in the electrical resistance with increasing annealing temperature for the glassy $Zr_{60}Al_{15}Ni_{25}$ alloy. The sample was prepared with $v_s=40$ m/s in Ar atmosphere and the measurement was performed in Ar atmosphere.

tive $d(R(T)/R_0)/dT$ remains to be still negative. This is responsible for the onset of the structural relaxation⁽⁴⁾ and will be mentioned later in Section IV. In the supercooled liquid region, the $d(R(T)/R_0)/dT$ is turned to a positive value and is almost linear with temperature (see also Fig. 2). It is likely predicted that the electron transport property is significantly changed after the glass transition occurs, although the reliable experimental evidence except for the electrical resistance and the specific heat (DSC) is not presented. The resistance curve responsible for the $Zr_{60}Al_{15}Ni_{7.5}Co_{2.5}Cu_{15}$ alloy is shown in Fig. 4 along with the inset. The behaviors of the electrical resistance below the glass transition are similar with those of the $Zr_{60}Al_{15}Ni_{25}$ alloy. The $d(R(T)/R_0)/dT$ becomes positive in the supercooled liquid region, similarly. However, the $d(R(T)/R_0)/dT$ changes clearly in the two steps as shown in the inset, where the first step ranges from T_g to about 765 K and the 2nd one ranges from 765 K to apparent crystallization temperature 775 K. After being heated to 761 and 771 K (shown in the inset with arrows), respectively, the samples were quickly cooled to room temperature and examined by X-ray diffraction.

Fig. 4 Change in the electrical resistance with increasing annealing temperature for the glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloy, along with the inset which shows the behavior around the supercooled liquid region.

Fig. 5 X-ray diffraction profiles for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ samples which were heated to 761 and 771 K, shown in Fig. 4 by the arrows.

The results are shown in Fig. 5. The profile of the sample heated to 771 K shows the existence of any crystallite and on the other hand any Bragg peaks are invisible for the sample heated to 761 K. This suggests that the crystallization starts from about 765 K for this alloy. However, the definite exothermic peak cannot be observed in the DSC thermogram⁽⁶⁾ around 765 K. Accordingly, the volume fraction of crystallized region is presumed to be significantly small.

Next, the effect of the thermal history on the stability of glassy alloy was examined. Figure 6 represents the effect of the quenching condition on the behavior of electrical resistance for the $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy, where the measurements were carried out in the Ar atmosphere. The behavior of the electrical resistance below T_g depends obviously on the quenching condition. This may be attributed to the difference in the amount of the quenched-in free volume contained. The $d(R(T)/R_0)/dT$ in the supercooled liquid region depends also weakly on the quenching rate. However, the T_g and T_x seem roughly to be independent on the quenching condition. In Fig. 7, the effects of the gas atmospheres in performing the measurements on the stability are displayed for the $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ (upper) and $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ (lower) alloys, where the samples prepared with $v_s=40$ m/s in the Ar atmosphere were used. The behavior of the electrical

Fig. 6 Effects of quenching condition on the behavior of electrical resistance for the glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy. The dot, solid line and dotted line represent respectively for the samples prepared with $v_s=40$ m/s in Ar, $v_s=40$ m/s in vacuum and $v_s=20$ m/s in Ar. All measurements were carried out in Ar atmosphere.

Fig. 7 Effects of gas atmosphere employed in measuring on the behavior of electrical resistance for the glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ (upper) and $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ (lower) alloys. The dot, solid line and dotted line show the results respectively obtained with Ar, He and vacuum atmospheres for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy. The solid and dotted lines are responsible for the results obtained with He and vacuum atmospheres for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloy.

resistance below T_g is almost independent of gas atmospheres employed. However, the behavior in the supercooled liquid region is dependent on the gas atmospheres. The $d(R(T)/R_0)/dT$ increases in the order of the values obtained in Ar, He and vacuum atmospheres, respectively. The amount of oxygen impurity in the atmospheres increases in the same order. It has previously been pointed out⁽⁶⁾ that the increment of the weight of glassy Zr-based alloys during annealing in the supercooled liquid region is due to the oxidation of the

Fig. 8 The bright field images of transmission electron microscope for (a) as-quenched and (c) heated $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ samples, and their SAD patterns (b) and (d), respectively.

samples. Figure 8 shows the bright-field transmission electron micrograph for the $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy which was heated to 750 K in the supercooled liquid region and then cooled quickly to room temperature. No crystalline phase is seen in the micrograph. On the other hand, it has been reported⁽¹²⁾ for the glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ and $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloys that the viscosity decreases and the elongation under constant load increases rapidly in the temperature range above glass transition. This suggests that the bonding between constituent atoms becomes weak after glass transition and the random thermal displacement of vibrating atoms increases in average. Therefore, it is presumed that the oxygen atom easily penetrates into the inner region from the sample surface. It has also been reported⁽¹³⁾ that the electronic density of state near Fermi level for glassy metals decreases by absorbing hydrogen atom because of the increase in the number of the chemical bonds between hydrogen and metallic atoms, leading to the increase in the electrical resistivity. A similar interpretation may be applied to the role of oxygen atom concerning the increase in resistivity in the supercooled liquid region for the present sample, though no clear evidence for the validity of the above-described prediction has been obtained so far. From the electrical resistance curves obtained under the different conditions, T_g and T_x are estimated and summarized in

Fig. 9 T_g and T_x estimated from the electrical resistance curves for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ samples. The horizontal axis represents the atmosphere employed in measuring. The solid symbols $\bullet$, $\blacksquare$ and $\blacktriangledown$ represent the samples in as-quenched states, prepared with $v_s=40$ m/s in Ar, $v_s=40$ m/s in vacuum and $v_s=20$ m/s in Ar, respectively. The open symbols are responsible for pre-heated samples (see also Fig. 12).

Fig. 9 for the $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy. The T_x values are in good agreement with each other within the experimental error. The T_g values seem to scatter slightly, but it is acceptable because the ambiguity to determine T_g should be taken into account. The $d(R(T)/R_0)/dT$ at 750 K, in the middle of the supercooled liquid region, was estimated and is plotted in Fig. 10 for the $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy. In a given gas atmosphere, this value is larger in the order of the samples produced with $v_s=40$ m/s in Ar, $v_s=40$ m/s in vacuum and $v_s=20$ m/s in Ar. On the other hand, under a given sample preparation condition, the influence of the environment in measuring $d(R(T)/R_0)/dT$ falls in the series: Ar>He>vacuum.

IV. Discussion

To examine the reproducibility of the glass transition, the samples were heated respectively to 755 and 760 K for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ and $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloys in the middle of the supercooled liquid region, and were cooled quickly to room temperature and subsequently heated again to 873 K. The results are shown in Fig. 11. For both samples, the glass transition phenomenon is reproduced obviously. However, the T_g seems to shift into higher temperature and T_x into lower one, compared to those for as-quenched samples. In the glass transition phenomenon of the amorphous alloy, it has been postulated⁽¹⁴⁾ that the glass transition temperature spreads due to the inherent topological disorder. However, the topological disorder can be decreased by heat treatment. The $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy sample was heated to 714 K just above T_g to decrease the topological disorder, and cooled quickly to room temperature and then heated again to 873 K. The results are shown in Fig. 12. The behavior in the range from 450 K to T_g shows a significant change,

Fig. 10 $d(R(T)/R_0)/dT$ at 750 K in the middle of the supercooled liquid region for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ samples.

Fig. 11 Reproducibility of the glass transition phenomena in glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ and $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloys. The samples were pre-heated to the temperatures in the middle of the supercooled liquid regions and then were cooled to the room temperature, and then were heated again to 873 K.

Fig. 12 Comparison of the behavior of electrical resistance for $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ samples in the as-quenched (dotted line) and pre-heated (solid line) states.

compared to that of the as-quenched sample, due to the partial annihilation of the quenched-in free volume. In addition, the slope $d(R(T)/R_0)/dT$ decreases slightly in the supercooled liquid region, compared to that of the as-quenched sample. However, T_g and T_x values are almost unchanged. Accordingly, higher T_g and lower T_x in the second heating in Fig. 12 suggest that a chemical ordering state which promotes the instability of present alloy is formed by annealing in the supercooled liquid region. As presented in previous section, the electrical resistance in the supercooled liquid region is sensitive to the thermal history, that is, the quenching condition and the atmosphere used in measuring. This suggests that the

oxygen impurity contained in the sample and/or in the atmosphere plays an important role. It has been reported that the oxide layer is formed on the surface of Zr-based amorphous alloys⁽⁶⁾⁽¹¹⁾. To check the fact, the Auger electron spectroscopy experiment was carried out for the as-quenched $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ sample which was prepared with $v_s=20$ m/s in Ar. The result is shown in Fig. 13, where the horizontal axis represents the number of sputtering operation to thin the sample, which corresponds roughly to the depth from the surface. The oxygen content is significantly high nearby the surface, and then decreases abruptly as a function of the distance from the surface. In contrast, the Ni and Zr contents are small nearby the surface, compared to the average content in the middle of the sample. Also, the Al content is almost unchanged throughout the sample. These facts may indicate that the Ni and Zr oxide layers are formed nearby the surfaces of the sample. Next, to decrease the influence of the surface oxide layer, the sample was polished mechanically till the depth of about $15\text{ }\mu\text{m}$ from the surfaces and the electrical resistance measurement was performed in vacuum. Figure 14 shows the results for the samples which were prepared with $v_s=20$ m/s in Ar (upper) and with $v_s=40$ m/s in vacuum (lower). The T_g , T_x and the slope $d(R(T)/R_0)/dT$ in the supercooled liquid region for the polished sample are similar with those of the as-quenched samples. This suggests that the oxygen atom is mainly supplied from the atmosphere instead of the oxygen layer on the surface. Also, it is noticeable that the slope is positive even for the sample in which the oxide layer was taken out by polishing and the electrical resistance was measured in the vacuum to suppress the oxygen impurity effect. Before we discuss whether the change in $d(R(T)/R_0)/dT$ is due to an inherent variation of electron transport property, the electron transport property of the present alloy system is briefly summarized. The electron transport properties of amorphous $(\text{Ni}_{33}\text{Zr}_{67})_{1-x}\text{Al}_x$ alloys below 300 K have been examined in details by Yamada *et al.*⁽¹⁵⁾⁽¹⁶⁾. Following their conclusion, Debye temperature θ_D for the $x=0.15$ alloy is 240 K. They have also postulat-

Fig. 13 Result of Auger electron spectroscopy for the as-quenched $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ sample which was prepared with $v_s=20$ m/s in Ar atmosphere. The signal intensities from O, Al, Ni and Zr atoms are exhibited as a function of the number of sputtering to thin the sample.

Fig. 14 Comparison of the behavior of electrical resistance for the as-quenched (solid line) and polished (dotted line) $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ samples which were prepared with $v_s=20$ m/s in Ar (upper) and $v_s=40$ m/s in vacuum (lower). The measurement was carried out in vacuum.

ed that the Hall coefficient at 300 K exhibits the positive value ($+4.2 \pm 0.7 \times 10^{-11} \text{ m}^3/\text{C}$). In addition, it has been generally pointed out⁽¹⁷⁾ that the mean free path of dominant carriers of high-resistivity alloys, in which the resistivity exceeds $200\text{--}250\text{ }\mu\Omega\text{ cm}$, is limited to the average atomic distance. We have confirmed that the glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ alloy possesses a high value ($210 \pm 10\text{ }\mu\Omega\text{ cm}$) of electrical resistivity at room temperature. Therefore, even if the present experiments are all performed in the high temperature range over θ_D , it is unreasonable to interpret the behavior of electrical resistance in the supercooled liquid region within the framework of generalized Faber Zimann theory. The increment of $d(R(T)/R_0)/dT$ in the supercooled liquid region may be intuitively interpreted by the mechanism in which the nano-crystalline clusters are formed during annealing and behave as a new scattering center for free carrier. However, this aspect, which is responsible for the diffraction model of free carrier, is conclusively invalid from brief inspection on the electron transport property for this alloy system. Instead, it is possibly postulated that the oxygen atom penetrating into the sample during annealing plays an important role in the electron transport property in this region.

It is remained unsolved whether or not the positive $d(R(T)/R_0)/dT$ in the supercooled liquid region is due to the inherent variation of electron transport property resulting from the phase transition from glassy solid to supercooled liquid. *In-situ* measurements of Hall coefficient, thermoelectric power and photoelectric spectroscopy in the supercooled liquid region will be needed to clarify the validity of the above-described concept.

V. Summary

The glassy $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ and $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{7.5}\text{Co}_{2.5}\text{Cu}_{15}$ alloys were typically chosen to examine the influence of the thermal histories on the thermal stability of these glassy alloys. The thermal behaviors of the sample were investigated mainly by the change in the electrical resistance. In the sample preparation, the quenching conditions were changed by the variation of the rotating velocity of the roller and the atmosphere in the quenching apparatus. In measuring the electrical resistance, the different gas atmospheres were employed. The conclusions obtained will be summarized as follows. (1) The reproductivity of the glass transition was confirmed by repeating the heat treatment across T_g . (2) As for the as-quenched samples, the T_g and T_x don't undergo a significant influence by the thermal history. (3) The behavior of the electrical resistance below T_g is unaffected by the thermal history of the sample, except for the effect of the quenched-in free volume. (4) The $d(R(T)/R_0)/dT$ in the supercooled liquid region depends remarkably on the thermal history of the sample. The $d(R(T)/R_0)/dT$ seems to be larger for the case where the sample is prepared and/or is measured with the environment containing more oxygen impurity. The result of Auger electron spectroscopy indicates that the oxide layer, possibly composed of nickel and zirconium ones, is formed nearby the surface of the sample. However, the TEM micrograph does not exhibit the existence of any crystallite in the sample within the resolution. (5) The validity of the occurrence of the positive $d(R(T)/R_0)/dT$ in the supercooled liquid region still remained unsolved due to the lack of the information about the electron transport property in this region. However, it is possibly postulated that an oxygen atom, penetrating into the sample from the atmosphere, makes a new chemical bond with a metallic atom and decreases the electronic density of state near Fermi energy, leading

to the increased electrical resistance.

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