Glass Transition and Viscoelastic Behaviors of La$_{55}$Al$_{25}$Ni$_{20}$ and La$_{55}$Al$_{25}$Cu$_{20}$ Amorphous Alloys

Hiroshi Okumura*, Akihisa Inoue** and Tsuyoshi Masumoto**

It has been found that amorphous La$_{55}$Al$_{25}$Ni$_{20}$ and La$_{55}$Al$_{25}$Cu$_{20}$ alloys exhibit a distinct glass transition and the temperature span between $T_g$ and $T_r (= T_c - T_g)$ exceeds 50 K. This is the first evidence for the formation of an amorphous phase with $\Delta T_r$ above 50 K in a metal-metal type system. With the aim of clarifying the glass transition behavior and the properties of supercooled liquid in the metal-metal type amorphous alloys, the changes in fundamental properties of specific heat ($C_p$), viscosity ($\eta$), tensile yield strength ($\sigma_t$), tensile elongation including elastic elongation ($\epsilon_e$) and viscoelasticity in the glass transition region were examined for both amorphous alloys. The transition brought about significant changes in the above-described properties, i.e., for the La$_{55}$Al$_{25}$Ni$_{20}$ alloy, an increase of $C_p$ by 12 J/mol K and $\epsilon_e$ from 2-43 to 188% and a dramatic decrease of $\eta$ to below $10^3$ Pa s and $\sigma_t$ from 710 to 3.47 MPa. In addition, the complex modulus decreased from 33.5 to 1.79 GPa and the loss tangent increased rapidly from $9 \times 10^{-3}$ to 3.22. Similar significant changes in the fundamental properties were also observed for another La$_{55}$Al$_{25}$Cu$_{20}$ amorphous alloy and hence these amorphous alloys were concluded to be typical glassy materials.

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I. Introduction

Recently, Inoue et al. have reported that lanthanide-Al base amorphous alloys such as the La–Al–Ni[11] and La–Al–Cu[31] systems exhibit a distinct glass transition below crystallization temperature. The largest temperature span $\Delta T_c (= T_c - T_r)$ between glass transition temperature ($T_c$) and crystallization temperature ($T_r$) reaches as large as 70 K for these amorphous alloys. The largest $\Delta T_c$ value is comparable to those for Pt–Ni–P and Pd–Ni–P[30] amorphous alloys. Consequently, the use of these alloys is expected to shed some light on clarification of an inherent nature of glass transition and supercooled liquid in metal-metal type amorphous alloys. The information on the glass transition appears to be essential for scientific and technological progresses of the new type amorphous alloys. It is generally known that the flow stress of an amorphous alloy decreases remarkably in the transition region from amorphous solid to supercooled liquid and the deformation mode changes from heterogeneous sliding to homogeneous viscous flow. Clarification of viscoelastic behavior of the metal-metal type amorphous alloys in the supercooled liquid region is very important for a better understanding of deformability into a given shape and consolidation into an amorphous bulk material. This paper is intended to clarify the changes in the fundamental properties such as specific heat, viscosity, tensile strength and viscoelasticity of La$_{55}$Al$_{25}$Ni$_{20}$ and La$_{55}$Al$_{25}$Cu$_{20}$ amorphous alloys in the glass transition region to the supercooled liquid.

II. Experimental Procedure

Ternary alloys with compositions La$_{55}$Al$_{25}$Ni$_{20}$ and La$_{55}$Al$_{25}$Cu$_{20}$ were used in the present study. The alloy compositions are nominally expressed in atomic per cent. Their ingots were prepared by arc-melting a mixture of pure La (99.9 mass%), Al (99.9 mass%) and Ni (99.9 mass%) or Cu (99.9 mass%) metals in a purified argon atmosphere. From the master alloy ingots, ribbons with a cross section of about 0.03 × 1 mm$^2$ were prepared by a single roller melt-spinning technique in an argon atmosphere. The amorphous nature of the melt-spun ribbons was examined by X-ray diffractometry (Rigaku RAD-B). The apparent specific heat ($C_p$) associated with structural relaxation, glass transition and crystallization was measured with a differential scanning calorimeter (Perkin-Elmer DSC-2). Tensile strength and elongation were measured by an Instron-type tensile testing machine at a strain rate of 5.56 $\times$ 10$^{-4}$ s$^{-1}$ at various temperatures from room temperature to 533 K.

Dynamic mechanical properties were measured by using a dynamic mechanical analyzer (Rheometrics RSA-II) with a forced oscillation mode. In a viscoelastic solid, oscillatory stress is delayed from supplied oscillatory strain by viscosity at an angle of $\delta$. Complex modulus ($E^*$) is the ratio of maximum stress to maximum strain and the real and imaginary parts of $E^*$ were defined as storage ($E'$) and loss ($E''$) moduli, respectively. The relation is schematically shown in Fig. 1. $E'$ is the value of the energy which is stored and recovered perfectly during one cycle of strain change, while $E''$ is the loss of energy which changes to heat during one cycle. The loss tangent (tan $\delta$) corresponds to the internal friction representing the degree of heat which was lost during oscillation[49-50].

* Graduate Student, Tohoku University, Sendai.
** Institute for Materials Research, Tohoku University, Sendai 980, Japan.
In this investigation, the temperature dependence of the $E^*$, $E^\ast$ and $\tan \delta$ was measured every 2 degrees at a constant oscillatory angular frequency of 62.8 rad/s and at a heating rate of 0.083 K/s. The oscillatory strain was changed in the range of 0.08 to 1.5 $\times$ 10^{-3}.

On the basis of the data obtained by a creep test using the RSA-II equipment, the coefficient of viscosity ($\eta$) was evaluated from eq. (1)\(^9\).

$$\eta = \sigma / \dot{\varepsilon} = \sigma_0 l_0 (1 + \Delta l/l_0)^2 (d\dot{l}/dt)^{-1}. \hspace{1cm} (1)$$

Here, $\sigma_0$ is the initial stress, $l_0$ the initial length of the sample, $\Delta l = l - l_0$ the elongation and $d\dot{l}/dt$ the creep rate at the secondary creep region. The time required for measurement was 600 s and $\sigma_0$ was in the range of 10 to 100 MPa.

III. Results and Discussion

1. Specific heat

Figure 2 shows the temperature dependence of $C_p$ for an amorphous La$_{35}$Al$_{13}$Ni$_{50}$ alloy. $C_{p,q}$ is the thermogram of the as-quenched sample and $C_{p,s}$ is that of the sample heated once to 500 K just above $T_s$. The scanning rate during heating and cooling was fixed to be 0.67 K/s. The $C_{p,q}$ value is about 22 J/mol·K around room temperature and begins to decrease at 340 K because of an irreversible structural relaxation. With increasing temperature, the $C_{p,q}$ shows a minimum value of 15.7 J/mol·K at 420 K, then increases rapidly in the glass transition region above 460 K and reaches 37.3 J/mol·K in the supercooled liquid around 520 K. With further increasing temperature, $C_{p,q}$ of the supercooled liquid decreases gradually and then rapidly due to crystallization. The $C_{p,s}$ is unaffected by thermal changes and consists of configurational contributions as well as those arising from purely thermal vibrations. As temperature rises, the $C_{p,s}$ increases linearly in the amorphous solid region and rapidly in the glass transition region and merges with $C_{p,q}$ in the supercooled liquid region. The $C_{p,q}$ represents the specific heat of the supercooled liquid with an internal equilibrium state. The difference between $C_{p,q}$ and $C_{p,s}$ manifests the irreversible structural relaxation which is presumed to arise from the annihilation of quenched-in “defects” and the enhancement of the topological and chemical short-range ordering\(^9\). When $T_q$ and $T_s$ are defined as each point of intersection of two tangent lines at the endothermic and exothermic peaks on the $C_p$, curve, the $T_q$ and $T_s$ values are measured to be 481 and 546 K, respectively, resulting in $\Delta T_s$ of 65 K. The increase in the specific heat caused by the glass transition ($\Delta C_{p,s-1}$) reaches 12 J/mol·K. The values of $\Delta T_s$ and $\Delta C_{p,s-1}$ are nearly equal to those of a Pt$_{40}$Ni$_{15}$P$_{25}$ amorphous alloy.
which is known\(^3\) to have the widest supercooled liquid region in metal-metalloid type amorphous alloys, indicating that the supercooled liquid has high stability against the nucleation and growth of a crystalline phase.

When the temperature dependence of the \(\Delta C_{p,s-1}\) shown in Fig. 2 is expressed to be the linear function of 29.8–3.33 \(\times\) \(10^{-3}\) T (J/mol·K) around \(T_s\) and the enthalpy (\(\Delta H\)), entropy (\(\Delta S\)) and free energy (\(\Delta G\)) of the amorphous solid at \(T_s\) (\(T_s\) = 481 K) are zero\(^9\), the relative changes in the \(\Delta H\), \(\Delta S\) and \(\Delta G\) as a function of temperature for the supercooled liquid are evaluated by eqs. (2), (3) and (4), respectively.

\[
\Delta H = \int \Delta C_{p,s-1} \, dT
\]
\[
\Delta S = \int \Delta C_{p,s-1} / T \, dT
\]
\[
\Delta G = \Delta H - T \Delta S.
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The \(\Delta H\), \(\Delta S\) and \(\Delta G\) manifest the difference in the thermodynamic properties between amorphous solid and supercooled liquid. Figure 3 shows the results calculated in the above-described condition. The resulting \(\Delta G\) has negative values in the entire temperature range except \(T_s\), implying that the free energy of the supercooled liquid is always lower than that of the amorphous solid. Accordingly, the transition from amorphous solid to supercooled liquid results in a decrease of free energy and the driving force of the transition (\(\Delta G\)) increases with an deviation of temperature from \(T_s\). However, the criterion for the appearance of the transition is also dependent on the relaxation time and/or atomic diffusivity. The relaxation time decreases significantly with increasing temperature and becomes short at temperatures above \(T_s\). Similarly, the atomic diffusivity increases drastically in the temperature range above \(T_s\). In addition, the negative value of the \(\Delta G\) increases with increasing temperature and hence the transition into the supercooled liquid is observed only in the temperature range between \(T_s\) and \(T_s\) in the conventional characterization methods with heating rates ranging from 0.033 to 1.33 K/s.

2. Viscosity

The significant increase in free volume at the glass transition is expected to cause a rapid decrease in viscosity. Figure 4 shows a thermal dilatometric curve of an amorphous \(\text{La}_{55}\text{Al}_{23}\text{Ni}_{20}\) alloy measured under an initial tensile stress of 0.32 MPa at a heating rate of 0.083 K/s. The elongation increases rapidly in the supercooled liquid region from 480 to 540 K. The temperature coefficient of expansion (\(\alpha\)) is estimated to be \(8.0 \times 10^{-3}\) K\(^{-1}\) for the amorphous solid and \(6.0 \times 10^{-4}\) K\(^{-1}\) for the supercooled liquid, indicating that the \(\alpha\) value increases by about 700% in the glass transition region. Figure 5 shows the temperature dependence of \(\eta\) for an amorphous \(\text{La}_{55}\text{Al}_{23}\text{Ni}_{20}\) alloy. The variation of \(\eta\) as a function of temperature can be divided into two regions of a larger \(\eta\) range from \(8.4 \times 10^{12}\) Pa·s to \(7.5 \times 10^{13}\) Pa·s at temperatures between 373 and 453 K and a smaller range from \(7.5 \times 10^{12}\) to \(2.9 \times 10^{11}\) Pa·s between 453 and 473 K. The variation in the \(\eta(T)\) behavior reflects the magnitude of the creep strain, resulting from the ease of atomic diffusivity in the steady state\(^{10}\). Furthermore, one can notice that the distinctive temperature of about 450 K agrees with the temperature at which \(C_p,s\) begins to deviate from \(C_p,s\), which does not contain the contribution of thermal history, as shown in Fig. 2.

3. Mechanical properties

Figure 6 shows the tensile yield stress (\(\sigma_y\)) and fracture elongation including elastic elongation (\(\varepsilon_f\)) as a function of temperature for an amorphous \(\text{La}_{55}\text{Al}_{23}\text{Ni}_{20}\) alloy.
curves at temperatures above 383 K. The yield point does not originate from the multiplication of dislocations which has been observed for common crystalline alloys and is thought to appear through a homogeneous deformation mode resulting from the viscous flow typical for an amorphous alloy. Accordingly, the temperature at which the yield point begins to appear seems to correspond to the onset temperature for the transition from inhomogeneous to homogeneous deformation. The $\sigma_y$ decreases rapidly two orders of magnitude at 473 K just below $T_g$ because of an increase in the contribution of the viscous flow.

On the other hand, the $\epsilon_f$ increases slightly from 2.43 to 3.48% in the temperature range between room temperature and 373 K and increases to 5.29% at about 383 K where the distinct yield phenomenon is observed. With a further increase of temperature, the $\epsilon_f$ increases gradually up to 450 K and significantly in the range from 463 K to $T_g$. As a result, the $\epsilon_f$ at $T_g$ ($\approx 481$ K) reaches 187% and shows a nearly constant value (≈ 190%) in the supercooled liquid region up to 500 K. The rapid increase in $\epsilon_f$ at 463 K just below $T_g$ is due to an increase in the contribution of the viscous flow resulting from the transition to the supercooled liquid phase. The decrease in $\epsilon_f$ at temperatures above 503 K originates from crystallization. Although the temperature dependence of $\epsilon_f$ corresponds well to that of $\sigma_y$, a slight difference is seen at the temperatures where the $\epsilon_f$ has a maximum value and the $\sigma_y$ has a minimum value. Considering that a partial crystallization occurs during long-time deformation at high temperatures near $T_g$, the slight difference is presumably because the influence of a small volume fraction of a crystalline phase on $\epsilon_f$ is different from that on $\sigma_y$.

An amorphous La$_{55}$Al$_{12}$Cu$_{30}$ alloy also shows a wide supercooled liquid region and the $T_g$, $T_x$ and $\Delta T_x$ values are measured to be 450 K, 504 K and 54 K, respectively. Although the $\Delta T_x$ exceeds 50 K for the La$_{55}$Al$_{12}$Cu$_{30}$ alloy, the value is slightly smaller than that of the La$_{55}$Al$_{12}$Ni$_{30}$ amorphous alloy. Figure 8 shows the temperature dependence of $\sigma_y$ and $\epsilon_f$ of the La$_{55}$Al$_{12}$Cu$_{30}$ amorphous alloy. The $\sigma_y$ decreases slightly from 701 to 691 MPa with increasing temperature from room temperature to 383 K and rapidly in the range of 393 K to $T_g$. 

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Fig. 5 Temperature dependence of viscosity of an amorphous La$_{55}$Al$_{12}$Ni$_{30}$ alloy.

Fig. 6 Changes in the yield stress and fracture elongation with testing temperature for an amorphous La$_{55}$Al$_{12}$Ni$_{30}$ alloy.

Here, the $\sigma_y$ value at temperatures below 373 K represents the tensile fracture stress. In addition, the change in the stress-strain curves with testing temperature is shown in Fig. 7. $\sigma_y$ is 710 MPa at room temperature and decreases gradually with increasing temperature. A distinct yield point is recognized on the stress-strain
The transition temperature ($T_p\approx 393$ K) corresponds to that ($T_p$) at which the yield point begins to appear. As a result, the $\sigma_t$ is as low as 24 MPa in the supercooled liquid region between $T_p$ and 463 K and then increases rapidly by crystallization. On the other hand, the $\varepsilon_f$ increases from 2.35% at room temperature to 6.46% at 393 K near $T_p$, followed by a rapid increase to 154% at 453 K in the supercooled liquid and then a rapid decrease resulting from crystallization. The changes of $\sigma_t$ and $\varepsilon_f$ in the glass transition region to the supercooled liquid for the La$_{55}$Al$_{15}$Cu$_{20}$ amorphous alloy are less significant as compared with those for the La$_{55}$Al$_{15}$Ni$_{20}$ amorphous alloy probably because of the smaller $\Delta T_c$ for the La$_{55}$Al$_{15}$Cu$_{20}$ alloy.

### 4. Viscoelasticity

Figure 9 shows the temperature dependence of $E^*$, $E''$ and $\tan \delta$ of the amorphous La$_{55}$Al$_{15}$Ni$_{20}$ alloy. $E^*$ decreases gradually from 33.5 GPa at room temperature to 28.9 GPa at 473 K and rapidly to 13.4 GPa at about 480 K because of the glass transition. The $E^*$ shows a plateau at temperatures between 491 and 503 K and then decreases rapidly to 1.79 GPa at 523 K. With further increasing temperature, $E^*$ increases significantly by crystallization. $E^*$ corresponding to the heat loss caused by a thermally activated process such as diffusion shows a peak at each temperature of 394, 483, 507 and 535 K. The lowest- and the highest-temperature peaks are associated with structural relaxation and crystallization, respectively. In the temperature range above the offset temperature of crystallization (541 K), no distinct change in $E''$ is seen because of the formation of a stable crystalline phase. The two peaks at 483 and 507 K in the glass transition region correspond to the two-stage reductions in $E^*$, suggesting the existence of distinguishable two relaxation processes. The details of these relaxation peaks are under investigation and will be described elsewhere. The large decrease of $E''$ to 8.5 GPa with increasing temperature from 507 to 527 K indicates that the transition to the supercooled liquid is complete, leading to an approach to an internal equilibrium state with very short relaxation times. The $\tan \delta$ associated with $E''$ shows a few peaks and the highest peak of 3.32 appears at 522 K where the $E^*$ shows a minimum value. The main peak with each shoulder at both sides corresponds to the second-stage glass transition peak of $E^*$ and the two shoulders result from the first-stage glass transition peak and crystallization peak, respectively.

Figure 10 shows the temperature dependence of $E^*$, $E''$ and $\tan \delta$ of the amorphous La$_{55}$Al$_{15}$Cu$_{20}$ alloy. The $E^*$ is 38.9 GPa at room temperature and decreases rapidly to 9.42 GPa at the first stage ranging from 450 to 465 K. Subsequently, it increases slightly at 483 K corresponding to the second stage and then rapidly due to crystallization. The $E^*$ shows each peak at 455 and 487 K, being different from the result for the amorphous La$_{55}$Al$_{15}$Ni$_{20}$ alloy in which three peaks in the $E^*(T)$ behavior are observed. The magnitude of the first peak
on the $E^*(T)$ curve is smaller than that of the second peak and the offset temperature of the first peak (465 K) is nearly equal to the offset temperature of the first stage on the $E^*(T)$ curve. In the temperature range of the second peak on the $E^*(T)$ curve, the second and the third (crystallization) stages are seen on the $E^*(T)$ curve. From the comparison of these data on $E^*(T)$ with $E^*(T)$, the second peak of $E^*$ at 487 K is due to the incorporation of two peaks of the second-stage relaxation at the glass transition and the crystallization. If either relaxation or crystallization occurs, $E^*(T)$ is expected to show a monotonous change with a single stage. A main peak with a peak intensity of 0.82 in the change of tan $\delta$ as a function of temperature is seen at 483 K which is equal to the offset temperature of the second-stage of $E^*(T)$, in addition to two shoulders at each temperature of 463 and 493 K. The good correspondence supports the appropriateness of the above-described interpretation.

The crystallization of the La$_{85}$Al$_{15}$Cu$_{30}$ amorphous alloy appears to start before the second relaxation due to the glass transition is complete, being different from that for the La$_{85}$Al$_{15}$Ni$_{30}$ alloy. The difference implies that the supercooled liquid of the La$_{85}$Al$_{15}$Ni$_{30}$ amorphous alloy has a higher stability against the nucleation and growth of a crystalline phase and can be translated to a higher degree of internal equilibrium state as compared with that for the La$_{85}$Al$_{15}$Cu$_{30}$ amorphous alloy, leading to the larger values of $\Delta T_c$ and tan $\delta$ and the larger decrease in $E^*$ for the La$_{85}$Al$_{15}$Ni$_{30}$ alloy. Consequently, the La$_{85}$Al$_{15}$Ni$_{30}$ amorphous alloy is concluded to be a more typical glassy material as compared with the La$_{85}$Al$_{15}$Cu$_{30}$ amorphous alloy.

IV. Summary

The glass transition behavior and the changes in specific heat, tensile strength and viscoelastic properties in the glass transition region were examined for amorphous La$_{85}$Al$_{15}$Ni$_{30}$ and La$_{85}$Al$_{15}$Cu$_{30}$ alloys exhibiting a significant supercooled liquid region. The results obtained are summarized as follows.

(1) The temperature interval of the supercooled liquid region is 65 K for La$_{85}$Al$_{15}$Ni$_{30}$ and 54 K for La$_{85}$Al$_{15}$Cu$_{30}$. The increase in specific heat in the glass transition region is about 12 J/mol·K for both alloys.

(2) Tensile strength and elongation change drastically by more than two orders in the transition region to the supercooled liquid state. These drastic changes are due to the change in the deformation mode from heterogeneous sliding to homogeneous viscous flow in the glass transition region.

(3) The two amorphous alloys have a high stability of supercooled liquid against the nucleation and growth of a crystalline phase. The fundamental data on specific heat, mechanical strength, elongation, deformation and viscoelasticity allow us to conclude that these amorphous alloys are a typical glassy material.

REFERENCES