

Al-La-Cu Amorphous Alloys with a Wide Supercooled Liquid Region

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Amorphous Al-La-Cu alloys exhibiting a wide supercooled liquid region and a high reduced glass transition temperature (T_g/T_m) were formed over a compositional range from 25 to 85 at% La and 0 to 60%Cu by melt spinning. The temperature span $\Delta T_x (= T_x - T_g)$ between T_g and crystallization temperature (T_x) reaches as large as 59 K for $\text{Al}_{20}\text{La}_{55}\text{Cu}_{25}$. The T_g/T_m is also as high as 0.68 for $\text{Al}_{20}\text{La}_{55}\text{Cu}_{25}$ and the Al-La-Cu alloys are concluded to have a high glass-forming ability. The T_x and hardness (H_v) increase with increasing Al and Cu contents in the range from 430 to 575 K and 140 to 300 and the tensile strength also has a similar compositional dependence in the range of 535 to 880 MPa. The compositional effect on T_x and H_v was presumed to originate from the variation of the atomic configuration which reflects the compounds of La_2Al , $\text{La}(\text{Al}, \text{Cu})$ and $\text{La}(\text{Al}, \text{Cu})_2$. The high stability of the supercooled liquid against the precipitation of crystalline phases in the vicinity of the stoichiometric composition $\text{Al}_1\text{La}_2\text{Cu}_1$, i.e., large ΔT_x and high T_g/T_m , seems to result from an optimum bonding state of the constituent atoms for the stoichiometric alloy.

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I. Introduction

It is of importance to accumulate systematic information on alloy compositions and fundamental properties of amorphous alloys exhibiting a wide supercooled liquid region before crystallization. The amorphous alloys with a supercooled liquid region in the temperature span above 50 K had been limited to noble metal-based alloy systems such as Pt-Ni-P, Pd-Ni-P, Pd-Cu-Si and Pd-Ni-Si⁽¹⁾. Most recently, Al-La-Ni amorphous alloys that do not contain any noble metals have been found⁽²⁾ to exhibit a wide supercooled liquid region with the temperature span between glass transition temperature (T_g) and crystallization temperature (T_x), $\Delta T_x (= T_x - T_g)$ reaching about 70 K. Furthermore, it has been clarified⁽³⁾ that an $\text{Al}_{25}\text{La}_{55}\text{Ni}_{20}$ amorphous alloy has a high reduced glass transition temperature (T_g/T_m) of 0.68 and can be obtained even by water quenching of the melt in a capillary with an inner diameter below about 1.2 mm. In a series of investigations on the formation of amorphous alloys exhibiting a wide supercooled liquid region in the Al-Ln-M (Ln=rare earth metal, M=transition metal) systems, the present authors found that Al-La-Cu amorphous alloys also exhibit a large ΔT_x value reaching 59 K. This paper is intended to clarify the composition range in which an amorphous phase in the Al-La-Cu system is obtained by melt spinning and compositional dependences of T_g , T_x , bending ductility, hardness and tensile fracture

strength of their amorphous alloys.

II. Experimental Procedure

Binary Al-La and La-Cu and ternary Al-La-Cu alloys were used in the present study. Their ingots were prepared by arc-melting a mixture of pure Al(99.99 mass%), La(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 0.02×1 mm 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 diffraction and transmission electron microscopy. 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 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 the 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 of 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. Vickers hardness (H_v) and tensile strength (σ_f) of the ribbon specimens were measured by a Vickers microhardness tester with a 0.98 N (100 gf) load and an Instron-type tensile testing machine at a strain rate of 4.17×10^{-4} s⁻¹, respectively. Methods of determining the H_v and σ_f have been described in ref. (4).

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III. Results

Figure 1 shows the composition range in which an amorphous Al-La-Cu phase is formed by melt spinning, along with the data on the bending ductility of the amorphous alloys. The glass formation range is rather wide and can be divided into two areas of Al-rich and La-rich compositions; 5 to 13 at% La and 0 to 7%Cu for the Al-rich alloys and 25 to 85%La and 0 to 60%Cu for the La-rich alloys. In addition, it is seen in Fig. 1 that binary amorphous alloys are formed in the Al-La and La-Cu systems. Figure 1 also shows that all the amorphous alloys have a good bend ductility which is shown by a 180 degree bending without fracture. This is different from the result for Al-La-Ni amorphous alloys that an approach of alloy composition to $(\text{Al, Ni})_2\text{La}$ brings about the transition from ductile to brittle nature. Figure 2 shows the compositional dependence of the onset temperature of crystallization (T_x) for the Al-La-Cu amorphous alloys. The T_x value for the La-rich amorphous alloys increases significantly with increasing Al and Cu contents and reaches 580 K for $\text{Al}_{35}\text{La}_{35}\text{Cu}_{30}$. As is evident from the contour lines of T_x in Fig. 2, the T_x values of the Al-La-Cu amorphous alloys are mainly dominated by the Al content and the effect of Cu appears to be considerably smaller than that of Al.

As examples, Fig. 3 shows the DSC curves of $\text{Al}_{45-x}\text{La}_{55}\text{Cu}_x$ ($x=15, 20$ and 25 at%) amorphous alloys. It is seen that the three alloys crystallize through a single stage accompanied by an exothermic peak. Furthermore, an endothermic reaction with a very wide temperature span is observed in the temperature range below the onset temperature of crystallization. For instance, the $\text{Al}_{20}\text{La}_{55}\text{Cu}_{25}$ amorphous alloy begins to transform from the amorphous solid to a supercooled liquid at about 441 K and keeps the supercooled liquid state in a wide

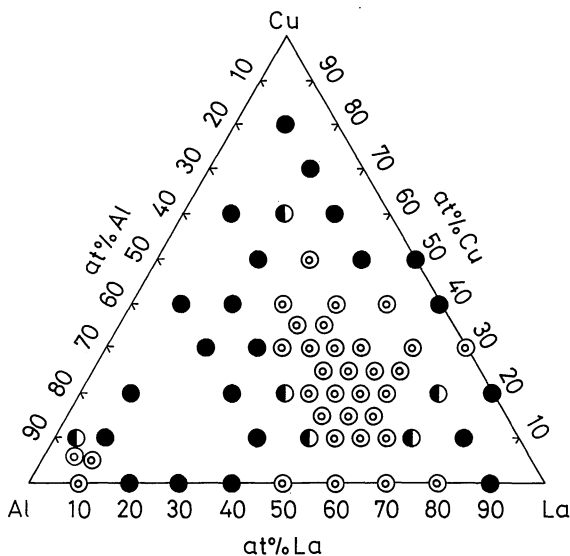


Fig. 1 Composition range for formation of amorphous phase in Al-La-Cu system: (⊙) amorphous (ductile); (◐) amorphous and crystalline; (●) crystalline.

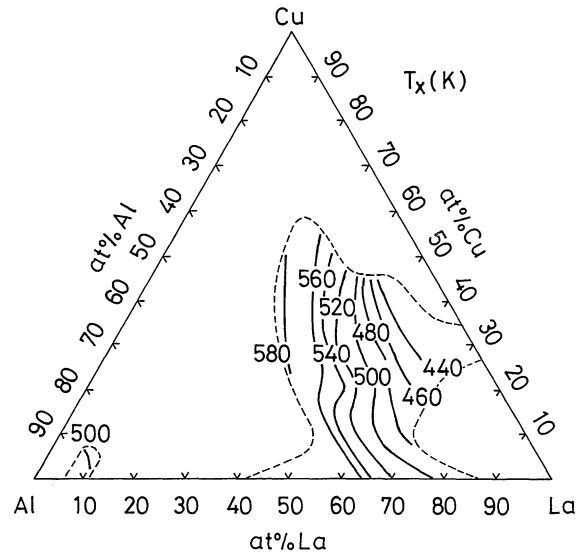


Fig. 2 Compositional dependence of crystallization temperature (T_x) of Al-La-Cu amorphous alloys.

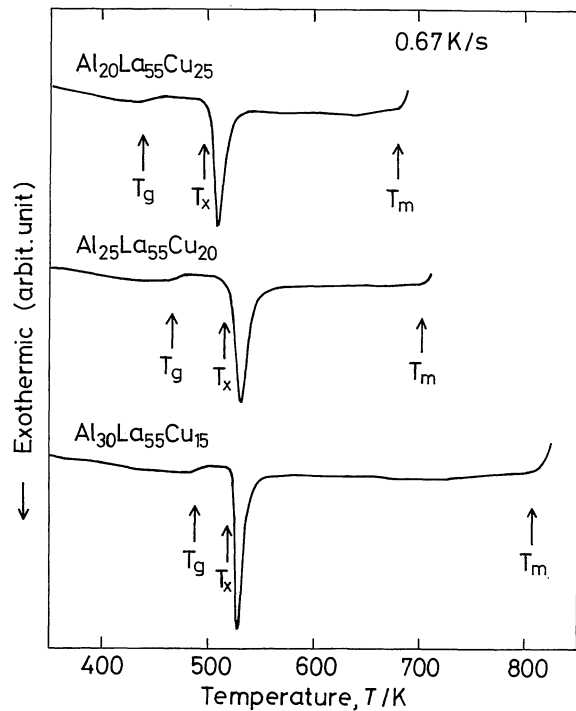


Fig. 3 Differential scanning calorimetric (DSC) curves of $\text{Al}_{45-x}\text{La}_{55}\text{Cu}_x$ ($x=15, 20$ and 25 at%) amorphous alloys.

temperature span reaching about 59 K, followed by crystallization at 500 K. As the largest temperature span of the supercooled liquid region for amorphous metallic materials is known to be about 65 K for Pt-Ni-P⁽⁵⁾, 60 K for Pd-Ni-P⁽⁵⁾, 58 K for Mg-Ni-La⁽⁶⁾ and 68 K for Al-Ni-La⁽²⁾, it is interpreted that the stability of the supercooled liquid against crystallization for the $\text{Al}_{20}\text{La}_{55}\text{Cu}_{25}$ alloy is nearly the same as those for the Pd-Ni-P and Mg-Ni-La alloys and lower than those for the Pt-Ni-P and Al-Ni-La alloys.

Figure 4 shows the compositional effect on the ΔT_x

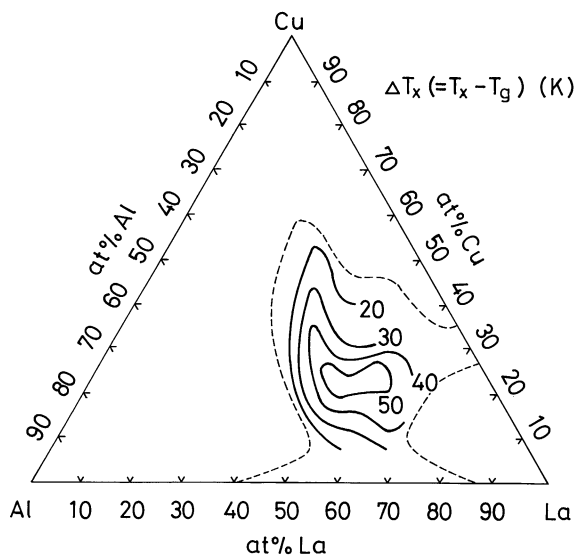


Fig. 4 Compositional dependence of the temperature span ΔT_x between T_g and T_x of Al-La-Cu amorphous alloys.

value for the Al-La-Cu amorphous alloys. The ΔT_x value is maximum (59 K) for $\text{Al}_{20}\text{La}_{55}\text{Cu}_{25}$ and decreases with a deviation from the alloy component. However, it is notable that the ΔT_x value above 50 K is obtained in the range from 45 to 60 %La and 18 to 27%Cu and the glass transition phenomenon is observed over a wide compositional range from 30 to 70%La and 5 to 50%Cu.

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 Al-La-Cu amorphous alloys. As an example, Fig. 5 shows the thermograms of an amorphous $\text{Al}_{25}\text{La}_{55}\text{Cu}_{20}$ alloy with the widest supercooled liquid region. The C_p value of the as-quenched phase is 24 J/mol·K near room temperature. As the temperature rises, the C_p value increases gradually and begins to decrease, indicating the onset of irreversible structural relaxation at 353 K. With a further increase in temperature, the C_p value shows its minimum at about 415 K, increases rapidly in the glass transition range from 440 to 475 K and reaches 38.0 J/mol·K for the supercooled liquid around 480 K. Above this temperature, the C_p value of the supercooled liquid decreases gradually and then rapidly due to crystallization at 506 K. It is seen in Fig. 5 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 11 J/mol·K. The difference in $C_p(T)$ between the as-quenched and the reheated state, $[\Delta C_p(T)]$, 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

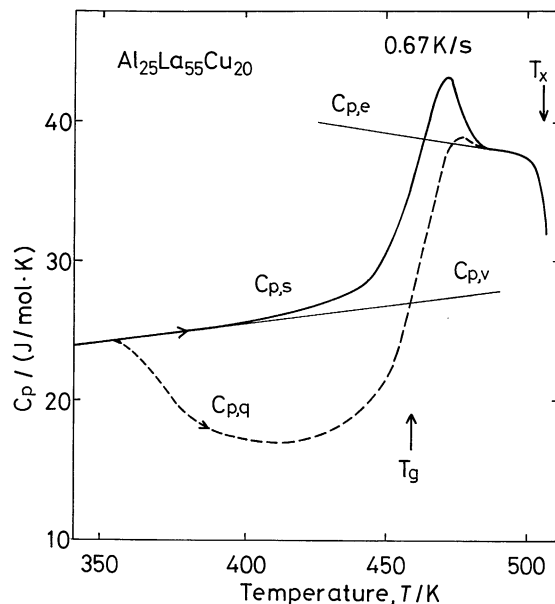


Fig. 5 The thermogram $C_{p,q}(T)$ of an amorphous $\text{Al}_{25}\text{La}_{55}\text{Cu}_{20}$ alloy in the as-quenched state. The solid line represents the thermogram $C_{p,s}(T)$ of the sample heated to 480 K.

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

$$C_{p,v} = 24.2 + 2.8 \times 10^{-2}(T - 350) \quad 350 \leq T \leq 430 \quad (1)$$

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. 5,

$$C_{p,e} = 37.2 + 4.0 \times 10^{-2}(500 - T) \quad 480 \leq T \leq 500 \quad (2)$$

The $\Delta C_{p,s \rightarrow l}$ value for the Al-La-Cu 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 11.5 J/mol·K in the vicinity of $\text{Al}_{20}\text{La}_{55}\text{Cu}_{25}$ and tends to decrease with a deviation from the alloy composition, being similar to the compositional dependence of ΔT_x . That is, there is a tendency that the larger the ΔT_x the larger is the $\Delta C_{p,s \rightarrow l}$. The $\Delta C_{p,s \rightarrow l}$ values are nearly equal to those for Pt-Ni-P⁽⁵⁾, Pd-Ni-P⁽⁵⁾, Mg-Ni-La⁽⁶⁾ and Al-La-Ni⁽²⁾ amorphous alloys.

It is important to examine the reduced glass transition temperature (T_g/T_m) for the Al-La-Cu amorphous alloys exhibiting the wide supercooled liquid region. As shown in Fig. 3, the onset temperature of fusion can be accurately measured from the DSC curve. When the onset temperature of the endothermic reaction in the temperature range above T_x is regarded as a melting temperature (T_m), the T_g/T_m value can be evaluated. The compositional effect on the T_g/T_m value for the Al-La-Cu

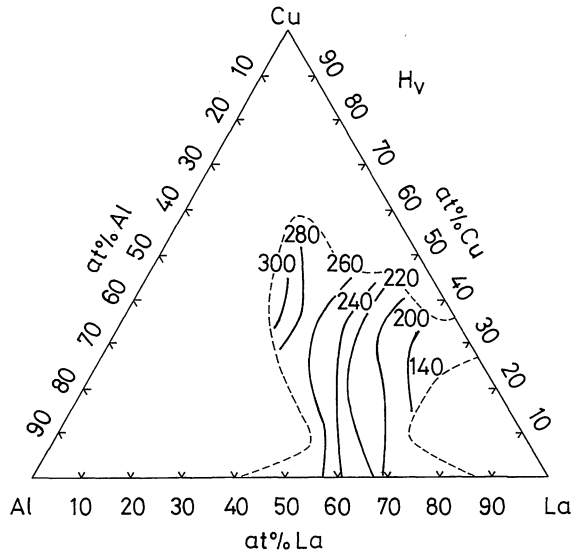


Fig. 6 Compositional dependence of Vickers hardness number (H_v) of Al-La-Cu amorphous alloys.

amorphous alloys is significant and the value is the largest (0.68) in the vicinity of 50%La and 25%Cu and decreases gradually with a deviation from the composition, e.g., 0.61 for $\text{Al}_{30}\text{La}_{55}\text{Cu}_{15}$ and 0.60 for $\text{Al}_{30}\text{La}_{50}\text{Cu}_{20}$. Thus, there is a clear tendency that the higher the T_g/T_m value, the larger are the ΔT_x and $\Delta C_{p,s \rightarrow l}$.

Vickers hardness (H_v) and tensile fracture strength (σ_f) were measured for the ductile Al-La-Cu amorphous alloys exhibiting large values of ΔT_x , $\Delta C_{p,s \rightarrow l}$ and T_g/T_m . Figure 6 shows the compositional effect on the H_v for the Al-La-Cu amorphous alloys. The H_v number is about 140 in the vicinity of 60%La and 30%Cu, increases significantly with increasing Al and Cu contents and reaches a maximum value of 300 in the vicinity of 35%Al and 35%Cu. Thus, the increase of the H_v value with an increase of Al and Cu contents is more remarkable in equiatomic compositions of Al/Cu \approx 1.0. The feature of the compositional effect on H_v is different from the tendency for T_g and T_x to increase remarkably with increasing Al content. A compositional effect similar to the T_x was also recognized for the σ_f and Young's modulus (E). As summarized in Table 1, the σ_f and E values increase with increasing Al content from 535 to 880 MPa and 29.0 to 42.7 GPa, respectively.

Table 1 Mechanical properties of Al-La-Cu amorphous alloys.

Alloy (at%)	σ_f (MPa)	E (GPa)	H_v	$\epsilon_{t,f} = \sigma_f/E$	$\epsilon_{c,y} \approx 9.8$ $H_v/3E$	$\sigma_{c,y} = 9.8$ $H_v/3$ (MPa)
$\text{Al}_{35}\text{La}_{55}\text{Cu}_{10}$	880	42.7	256	0.021	0.020	836
$\text{Al}_{30}\text{La}_{50}\text{Cu}_{20}$	750	37.7	240	0.020	0.021	784
$\text{Al}_{25}\text{La}_{55}\text{Cu}_{20}$	600	31.9	213	0.019	0.022	696
$\text{Al}_{25}\text{La}_{50}\text{Cu}_{25}$	535	29.0	208	0.018	0.023	679

Tensile fracture strength (σ_f), Young's modulus (E), Vickers hardness (H_v), tensile fracture strain ($\epsilon_{t,f} = \sigma_f/E$), compressive yield strain ($\epsilon_{c,y} \approx 9.8 H_v/3E$) and compressive yield strength ($\sigma_{c,y} \approx 9.8 H_v/3$).

IV. Discussion

1. Compositional effect on T_x , H_v , E and σ_f

It was shown in section III that the T_x , H_v , E and σ_f values of the Al-La-Cu amorphous alloys increased with increasing Al and Cu contents. It is thus interpreted that the simultaneous existence of the solute elements (Al and Cu) in the La-based amorphous alloys brings about the increase in T_x , H_v , E and σ_f . Although there is no equilibrium phase diagram available in the Al-La-Cu ternary alloys, the binary phase diagrams of La-Al⁽⁷⁾ and La-Cu⁽⁸⁾ alloys indicate that the increase in T_x , H_v , E and σ_f corresponds well to the significant increase in T_m from 823 to 1678 K for the La-Al system and from 748 to 1103 K for the La-Cu system, accompanied by the structural changes of $\text{La}_3\text{Al} \rightarrow \text{LaAl} \rightarrow \text{LaAl}_2$ and $\text{LaCu} \rightarrow \text{LaCu}_2$. From the similarities of the chemical formula and crystal structure of their compounds in the La-Al and La-Cu systems, it is reasonable to consider that the compounds in the Al-La-Cu ternary system change in the order of $\text{La}_3\text{Al} + \text{LaCu} \rightarrow \text{La}(\text{Al}, \text{Cu}) \rightarrow \text{La}(\text{Al}, \text{Cu})_2$ with increasing Al and Cu contents, accompanied by the significant increase in T_m . This presumption is supported from the result⁽⁹⁾ that a primary crystalline phase in the crystallization process of $\text{Al}_{25}\text{La}_{50}\text{Cu}_{25}$ amorphous alloy consists of an orthorhombic phase which has the same crystal structure as that for $\text{LaAl}^{(10)}$ and $\text{LaCu}^{(11)}$ compounds. Although the amorphous structure of the Al-La-Cu alloys remains unclear, it is presumed that the atomic configuration on a short-range scale varies with the sequent change in the equilibrium compounds. That is, the amorphous structure reflects the La_3Al and LaCu with low T_m in the La-rich compositional range and the increase in the Al and Cu contents gives the variation into the amorphous structure which reflects the $\text{La}(\text{Al}, \text{Cu})$ and $\text{La}(\text{Al}, \text{Cu})_2$ compounds with higher T_m . Accordingly, the monotonous and significant increases in T_x , H_v , E and σ_f with Al and Cu contents may be explained by the variation of the short-range atomic configuration which reflects the change of the equilibrium compounds of $\text{La}_3\text{Al} + \text{LaCu} \rightarrow \text{La}(\text{Al}, \text{Cu}) \rightarrow \text{La}(\text{Al}, \text{Cu})_2$. The entire replacement between Al and Cu for the LaM and LaM_2 seems to be possible in the rapidly solidified state because of the similar types of the chemical formula and crystal structure of the two compounds between the La-Al⁽⁷⁾ and La-Cu⁽⁸⁾ systems. It is to be expected from a common concept of the strengthening of solid solution that the achievement of the entire replacement gives a maximum value of H_v in an equiatomic compositional range of Al and Cu. On the other hand, the highest T_x value was obtained at an Al-rich composition in the high solute concentration range, being slightly different from the composition of the highest H_v value. The discrepancy is presumably due to the fact that the melting temperature of Al_2La is about 1.6 times as high as that ($T_m = 1088$ K) of Cu_2La .

2. Compositional effect on ΔT_x and T_g/T_m

The supercooled liquid region at temperatures below T_x was observed in a wide compositional range of 30 to 70%La and 5 to 50%Cu. It is particularly notable that the temperature span (ΔT_x) of the supercooled liquid is as large as 59 K in the vicinity of 55%La and 25%Cu. Furthermore, it is shown that the amorphous alloys with the large ΔT_x values have high T_g/T_m values reaching about 0.68. The large values of ΔT_x and T_g/T_m indicate that the supercooled liquid of the Al-La-Cu amorphous alloys has a high stability to the nucleation and growth of the crystalline phases. The retardation of the transformation to a crystalline phase for the supercooled liquid is thought to bring about the high values of ΔT_x and T_g/T_m . The reason why the large values of ΔT_x and T_g/T_m are obtained in the vicinity of $\text{Al}_{25}\text{La}_{50}\text{Cu}_{25}$ is discussed in this section. The equilibrium phase diagrams of La-Al⁽⁷⁾ and La-Cu⁽⁸⁾ binary alloys show the existence of a deep trough in the vicinity of 70%La, indicating a high stability of the liquidus structure at their alloy compositions. The ratios of Al to La and Cu to La at the compositions are nearly equal to those for the $\text{Al}_{25}\text{La}_{50}\text{Cu}_{25}$ alloy with the largest ΔT_x and T_g/T_m values. The agreement suggests that the liquidus structure is more stable in the vicinity of $\text{Al}_{25}\text{La}_{55}\text{Cu}_{20}$. The existence of the deep trough suggests an ease of obtaining a supercooled state at 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 a number of eutectic-type alloy systems have an easy supercooling capacity of liquid, no amorphous alloys with large ΔT_x have been obtained in most of the eutectic-type alloys⁽¹²⁾. The exceptionally high stability of the supercooled liquid in the Al-La-Cu system seems to be attributed to the unique bonding state of the Al-La-Cu amorphous alloys. The electronic structure and bonding nature of the Al-La-Cu amorphous alloys are also under investigation.

3. Glass-forming capacity

As described above, the large ΔT_x 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 have a high resistance to the nucleation and growth of crystalline phases, leading to a high glass-forming capacity, though the origin for the high resistance of the Al-La-Cu alloys remains unknown. It is known that the T_g/T_m value is closely related to the glass-forming capacity and the higher the T_g/T_m value the larger is the glass-forming capacity. The empirical relation⁽¹³⁾ between T_g/T_m and the maximum cooling rate for the formation of an amorphous phase allows us to evaluate that the minimum cooling rate for the $\text{Al}_{20}\text{La}_{55}\text{Cu}_{25}$ alloy is as small as about 10^2 K/s. The cooling rate is almost comparable to that which can be achieved even by water quenching, suggesting the

possibility of obtaining an amorphous bulk by water quenching. The possibility has been confirmed by the evidence⁽¹⁴⁾ that an amorphous $\text{Al}_{25}\text{La}_{50}\text{Cu}_{25}$ alloy with a cylindrical form in the diameter range below 0.8 mm is formed by water quenching.

The high T_g/T_m value also implies that the viscosity of the supercooled liquid can reach about 10^{12} N·s/m² 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. The difficulty of diffusivity is thought to take place by the achievement of a tight bonding state of the constituent atoms. Considering that the alloys exhibiting the largest values of ΔT_x and T_g/T_m are located in the vicinity of $\text{Al}_{25}\text{La}_{50}\text{Cu}_{25}$ (AlLa_2Cu), the short-range atomic configuration which reflects the stoichiometric $\text{Al}_1\text{La}_2\text{Cu}_1$ compound may be favorable for the suppression of the diffusivity of the constituent atoms. Research of the atomic configuration of the $\text{Al}_1\text{La}_2\text{Cu}_1$ amorphous alloy with a stoichiometric composition is expected to shed some light on the clarification of the mechanism for the appearance of large values of ΔT_x and T_g/T_m .

V. Summary

In order to find amorphous alloys exhibiting a glass-forming capacity, a wide supercooled liquid region and high mechanical strengths in Al-containing system by liquid quenching, the rapidly solidified structure in the Al-La-Cu ternary system was examined over a wide compositional range. The amorphous alloys are formed in two compositional ranges which are located in the Al-rich composition of 5 to 13%La and 0 to 7%Cu and in the La-rich composition of 25 to 85%La and 0 to 60%Cu. Furthermore, the Al-La-Cu amorphous alloys exhibit a supercooled liquid region in the La-rich composition range of 30 to 70%La and 5 to 50%Cu. In particular, the alloys which are located in the vicinity of 55%La and 25%Cu have large temperature spans ΔT_x ($=T_x - T_g$) reaching about 59 K and high T_g/T_m values above 0.6. The large values of ΔT_x and T_g/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 degree of supercooling. The high stability of the supercooled liquid and the steep increase of viscosity are explained by the assumption that the amorphous structure is in an optimally bonding state which reflects the stoichiometric compound $\text{La}_2\text{Al}_1\text{Cu}_1$. The T_x and H_v of the La-rich amorphous alloys increase from 430 to 575 K and 140 to 300 with increasing Al and Cu contents and the increase is more remarkable at an equiatomic composition of Al and Cu for H_v and at an Al-rich composition for T_x . The E and σ_f values also show a compositional effect similar to that for T_x and the highest σ_f value is 880 MPa. The compositional effect on T_x , H_v , E and σ_f is presumed to result from the change in the short-range atomic configuration which reflects the sequent change of

the equilibrium compounds of $\text{La}_3\text{Al} + \text{LaCu}$, $\text{La}(\text{Al}, \text{Cu})$ and $\text{La}(\text{Al}, \text{Cu})_2$ because the decomposition temperature of the compounds increases from 820 to 1678 K in the order of La_3Al , LaAl and LaAl_2 and from 798 to 1103 K in the order of LaCu and LaCu_2 .

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