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Grain growth kinetics in a supercooled liquid region of $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ metallic glasses

J. SAIDA, C. LI, M. MATSUSHITA
Inoue Superliquid Glass Project, ERATO, Japan Science and Technology Corporation (JST), Sendai 982-0807, Japan
E-mail: jsaida@sendai.jst.go.jp

A. INOUE
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The grain growth kinetics of a Zr_2Cu crystalline phase in a supercooled liquid region of $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ metallic glasses was examined at different temperatures. Since no significant changes in the constitution and strain in Zr_2Cu phase were seen for the annealed samples, the grain size calculated from a half value width of the X-ray diffraction peak by Scherrer's formula was used. The grain growth is controlled by a single kinetics with a thermal activation process of Arrhenius type, which is described by

$$D^3 - D_0^3 = k_0\, t_g \exp\left(-\frac{Q}{RT_a}\right).$$

The activation energy for the grain growth of Zr_2Cu is 165 ± 10 kJ mol^{-1} for $Zr_{65}Cu_{27.5}Al_{7.5}$ and 440 ± 30 kJ mol^{-1} for $Zr_{65}Cu_{35}$. The lower activation energy in the ternary glass is attributed to the mechanism of which the crystallization and grain growth are dominated by redistribution of only Al, while the much higher activation energy might reflect the difficulty of the diffusion of Zr with larger atomic size in the binary glass. It is concluded that the difference in the grain growth mechanism is an important factor of stabilizing the glassy state. © *2000 Kluwer Academic Publishers*

1. Introduction

It has recently been found that new metallic glasses in a number of metal-metal systems such as Mg-TM-Ln [1], Ln-TM-Al [2] and Zr-TM-(Al) [3, 4] (TM = transition metal, Ln = lanthanide metal) have a wide supercooled liquid region before crystallization. Among these metallic glasses, the Zr-TM-Al alloys are particularly interesting because of their extremely wide supercooled liquid region exceeding 100 K [5, 6]. In the Zr-based ternary alloy system, the temperature interval of the supercooled liquid region shows a maximum value of about 90 K for the $Zr_{65}Cu_{27.5}Al_{7.5}$ alloy [7]. It has already been reported structural analysis [8], thermal stability [9] and crystallization kinetics [10–12] in supercooled liquid and amorphous states of the $Zr_{65}Cu_{27.5}Al_{7.5}$ metallic glass. Inoue *et al.* has pointed out that the appearance of the wide supercooled liquid region has been attributed to the difficulty of precipitation of crystalline phases resulting from the large solid-liquid interfacial energy and the suppression of growth resulting from the necessity of long-range redistribution of Al at the solid-liquid interface [13]. The authors have reported that a metastable ZrAl phase is observed at the initial crystallization stage, in addition to a main b.c.t. $Zr_2(Cu, Al)$ phase [14]. The lattice spacing and grain size of the Zr_2Cu phase change significantly by the disappearance of ZrAl, implying that Al has an important role in the growth reaction of Zr_2Cu. Moreover, the grain growth behavior was also examined for the $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ metallic glasses [15]. It is clarified that the growth rate of the Zr_2Cu phase in the isothermal heat treatment between two metallic glasses has a significant difference. While the Zr_2Cu in the binary glass starts to grow at the annealing temperature just above glass transition temperature, T_g and the size increases rapidly with further increasing temperature, the growth rate in the ternary glass is quite slow even at the temperature just below crystallization temperature, T_x. These results indicate that the grain growth in the ternary glass is dominated by the redistribution of Al deconvoluted from the ZrAl primary phase, which is an important factor of the stabilization of supercooled liquid and the degradation of grain growth reaction. This study is intended to investigate the grain growth kinetics of the Zr_2Cu phase during crystallization from the supercooled liquid region for the $Zr_{65}Cu_{27.5}Al_{7.5}$ and

$Zr_{65}Cu_{35}$ metallic glasses and clarify the effect of Al on the precipitation and grain growth of the crystalline phase and the reason for the high stability of the supercooled liquid against crystallization.

2. Experimental procedure

Ternary $Zr_{65}Cu_{27.5}Al_{7.5}$ and binary $Zr_{65}Cu_{35}$ alloys were examined in the present study. The prealloyed ingots were prepared by arc-melting a mixture of pure metals in a purified Ar atmosphere. The compositions are nominally expressed in atomic percent. The amorphous alloy ribbon was prepared by a single roller melt-spinning technique in an Ar atmosphere. The T_g and T_x of as-quenched samples are determined to be 646 K and 731 K, respectively for $Zr_{65}Cu_{27.5}Al_{7.5}$ and 624 K and 678 K, respectively for $Zr_{65}Cu_{35}$ by the differential scanning calorimeter analysis at a heating rate of 0.67 K s^{-1}. The amorphous ribbon was annealed at a heating rate of 0.67 K s^{-1} for various times in a temperature range of 700 K to 730 K for $Zr_{65}Cu_{27.5}Al_{7.5}$ and 640 K to 660 K for $Zr_{65}Cu_{35}$ and the growth of a crystalline phase from a supercooled liquid region was examined. The annealed samples were examined by X-ray diffractometry with Cu K_α radiation at 40 kV-30 mA at a scanning speed of 0.03° s^{-1} to determine a crystalline phase and line-broadening. The grain size for the isothermal annealed samples was measured by X-ray line-broadening using Scherrer's formula [16].

3. Results and discussion

Fig. 1 shows the change in the X-ray diffraction patterns of the $Zr_{65}Cu_{27.5}Al_{7.5}$ alloy with annealing times, t_a at 700 K. A ZrAl phase is seen in addition to the Zr_2Cu phase. The authors have pointed out the strong relationship between the grain growth of Zr_2Cu and the deconvolution of ZrAl phase [14]. The grain growth analysis was made under the condition of mixed of Zr_2Cu and ZrAl phases for $Zr_{65}Cu_{27.5}Al_{7.5}$. On the other hand, the $Zr_{65}Cu_{35}$ crystallizes through a single Zr_2Cu phase. As shown in Fig. 1, the intensity of the X-ray diffraction peak of Zr_2Cu phase increases with increasing annealing time, while the width of line-broadening decreases, suggesting that the grain growth takes place. Since the line-broadening is dominated by three factors of grain size, constituent and strain, it is necessary that the contribution of constituent and strain of the Zr_2Cu phase must be considered to evaluate a true grain size. The changes in the lattice spacing of Zr_2Cu (103) with annealing time, t_a at various temperatures for $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ are shown in Fig. 2. The lattice spacing of Zr_2Cu for $Zr_{65}Cu_{27.5}Al_{7.5}$ is larger than that for $Zr_{65}Cu_{35}$ because of the dissolution of Al into Zr_2Cu. No significant change in the lattice spacing with annealing time and temperature is seen for these metallic glasses, indicating that the Al content of Zr_2Cu phase in $Zr_{65}Cu_{27.5}Al_{7.5}$ remains unchanged under the annealing conditions. In order to evaluate the strain factor for the line-broadening, Hall's formula is used [17], which is described by

$$B\cos\theta_B = \frac{0.94\lambda}{D_t} + 2\varepsilon\sin\theta_B, \qquad (1)$$

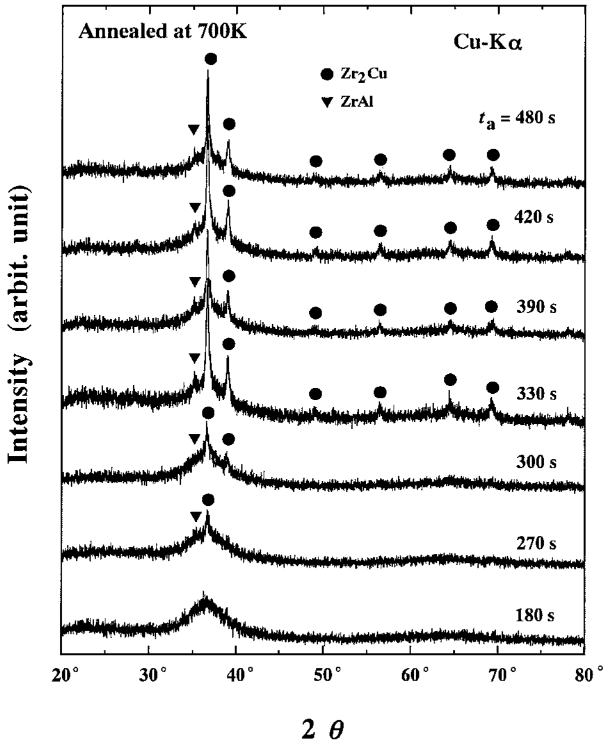

Figure 1 X-ray diffraction patterns of the annealed samples with various times at 700 K for the $Zr_{65}Cu_{27.5}Al_{7.5}$ metallic glass.

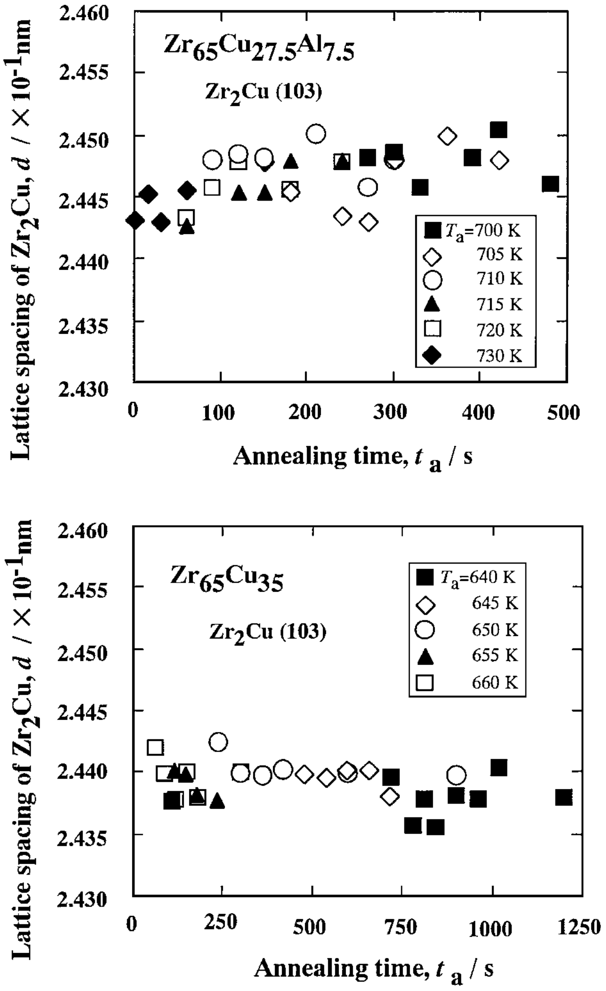

Figure 2 Change in the lattice spacing of Zr_2Cu (103) with annealing time, t_a for the $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ metallic glasses.

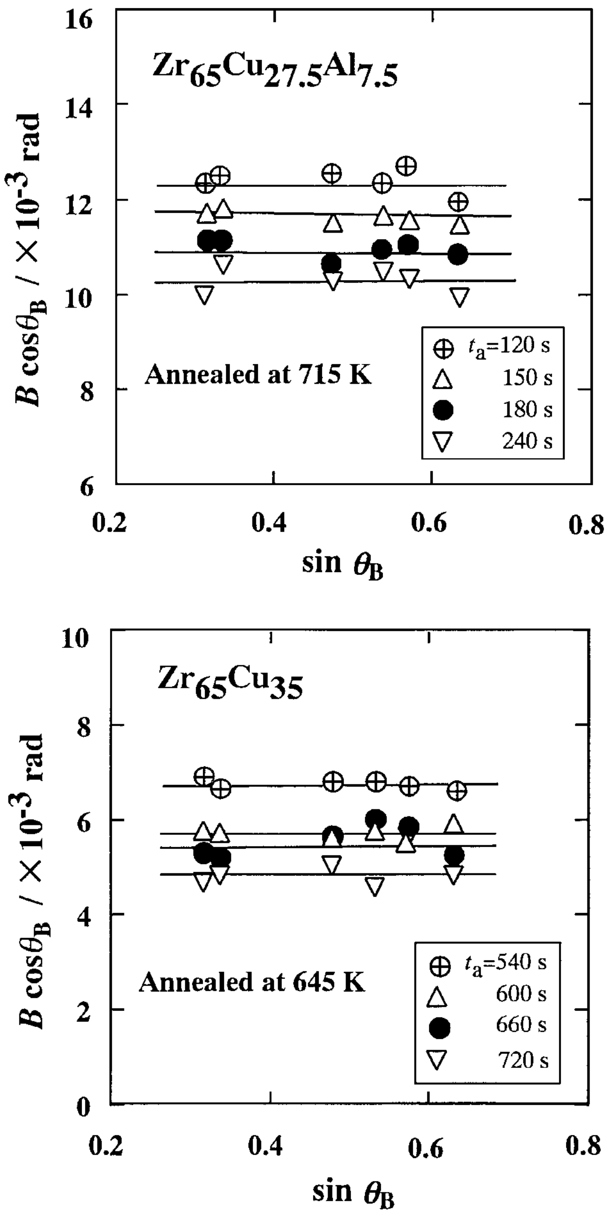

Figure 3 $B \cos\theta_B$ versus $\sin\theta_B$ with various annealing times, t_a for $Zr_{65}Cu_{27.5}Al_{7.5}$ annealed at 715 K and $Zr_{65}Cu_{35}$ annealed at 645 K.

where B is the line-broadening width obtained from half-value width of Zr_2Cu peak, θ_B is Bragg angular, λ is wavelength of X-ray, ε is plastic strain and D_t is true grain size. The D_t is obtained by eliminating the second strain term in Equation 1 and by extrapolating the curve of $B \cos\theta_B$ versus $\sin\theta_B$ to $\theta_B = 0$ [18]. Examples of this exercise for various planes are shown in Fig. 3. The line-broadening data were obtained for $Zr_{65}Cu_{27.5}Al_{7.5}$ annealed at 715 K for 120 s to 240 s and for $Zr_{65}Cu_{35}$ annealed at 645 K for 540 s to 720 s. All these curves yield a linear relation with a slope of approximately 0, indicating that the strain term can be ignored. Therefore, the grain size calculated from the line-broadening of (103) plane can be regarded as a true grain size of Zr_2Cu. Fig. 4 shows the change in the grain size of the $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ glasses with grain growth time, t_g defined as follows:

$$t_g = t_a - t_0, \tag{2}$$

where t_0 is the time identified from the peak first in the X-ray diffraction pattern during isothermal annealing.

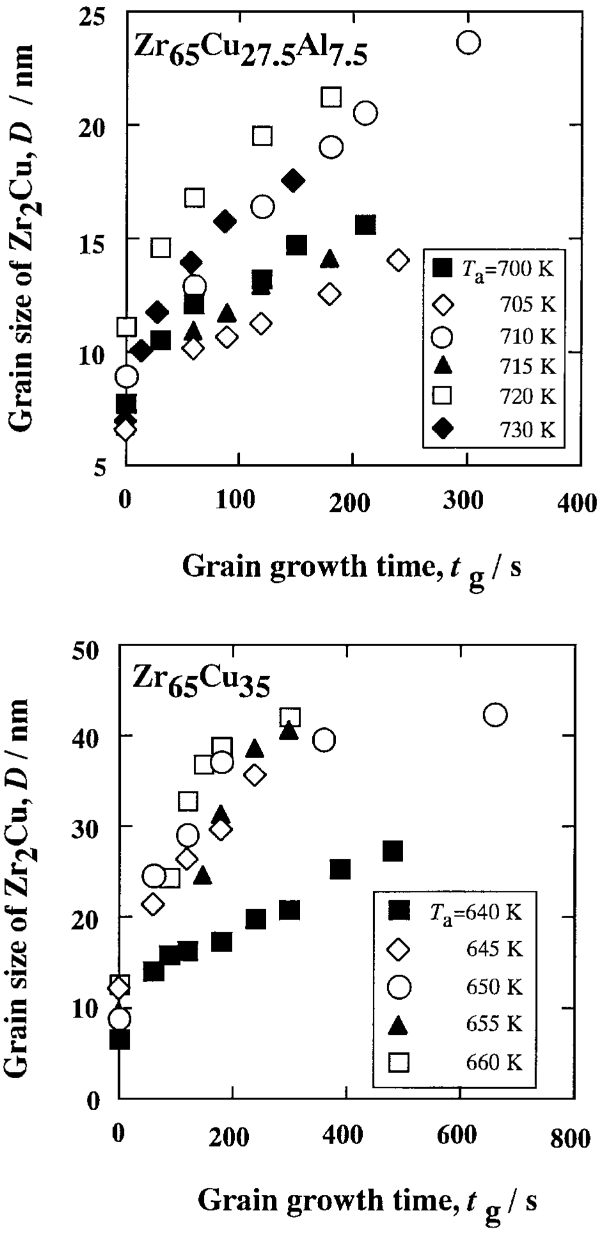

Figure 4 Change in the grain size of Zr_2Cu with grain growth time, t_g at various temperatures for the $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ metallic glasses.

The grain size increases monotonously with increasing t_g. The grain sizes obtained by transmission electron microscopy are in agreement with those calculated by Scherrer's formula [15]. Fig. 5 shows the relationship between grain growth time, t_g and cube of grain size which has the same dimension as the volume of crystalline particles in the $Zr_{65}Cu_{27.5}Al_{7.5}$ glass. A good linear relation is seen between two parameters, i.e. the volume of crystalline particle increases linearly with growth time. These data allow us to conclude that the grain growth for the present samples obeys a thermal activation process of Arrhenius type, which implies the grain growth process by the movement of individual atom. Considering the grain growth behavior as shown in Fig. 4, a growth law can be described by [19, 20]

$$D = k' t_g^n \tag{3}$$

or

$$D^N = k t_g, \tag{4}$$

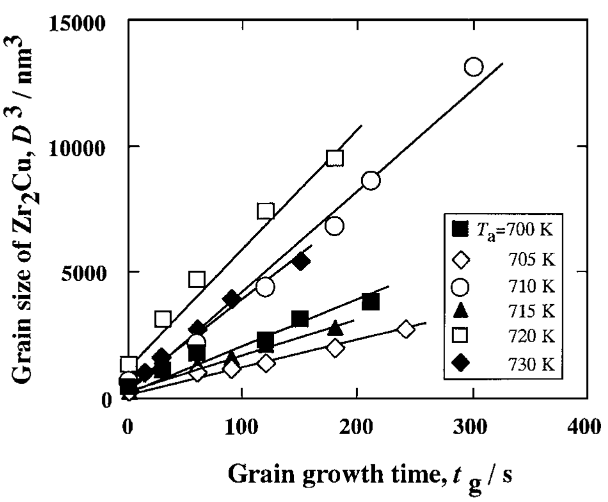

Figure 5 Relationship between the cube of grain size of Zr_2Cu and grain growth time, t_g at various temperatures for the $Zr_{65}Cu_{27.5}Al_{7.5}$ metallic glass.

where k or k' are the growth constants, n is the time exponent which is connected to N by the relation of $N = n^{-1}$. By differentiating Equation 4 with respect to time, t_g, one obtains

$$\left(\frac{dD}{dt_g}\right) = \frac{k}{ND^{N-1}}, \tag{5}$$

which is led to the following equation by taking the logarithm of Equation 5,

$$\ln\left(\frac{dD}{dt_g}\right) = \ln\left(\frac{k}{N}\right) - (N-1)\ln D. \tag{6}$$

Therefore, the plot of the logarithm of (dD/dt_g) against the logarithm of D should give a slope of $-(N-1)$ or $(1 - n^{-1})$.

The logarithm of grain growth rate, (dD/dt_g) taken as the tangent on the respective curves shown in Fig. 4 is then plotted against the logarithm of grain size for $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ in Fig. 6. All the curves yield straight lines, suggesting that the grain growth is controlled by the same kinetics. The slopes of these straight lines are shown in Fig. 7. The straight lines have almost identical slope of -2 ± 0.1 for $Zr_{65}Cu_{27.5}Al_{7.5}$ and -2 ± 0.2 for $Zr_{65}Cu_{35}$, respectively, revealing that the grain growth in this temperature range is controlled by a single kinetic. From Fig. 7, the kinetics equation can be obtained as follows:

$$\ln\left(\frac{dD}{dt_g}\right) = \ln\left(\frac{k}{3}\right) - 2\ln D. \tag{7}$$

By integrating the above Equation 7 with respect to time, t_g, one obtains

$$D^3 - D_0^3 = kt_g. \tag{8}$$

Here, D_0 is the crystallite size at $t_g = 0$ and the rate constant k depends on temperature in the Arrhenius relation, so that it is written as

$$k = k_0 \exp\left(-\frac{Q}{RT_a}\right), \tag{9}$$

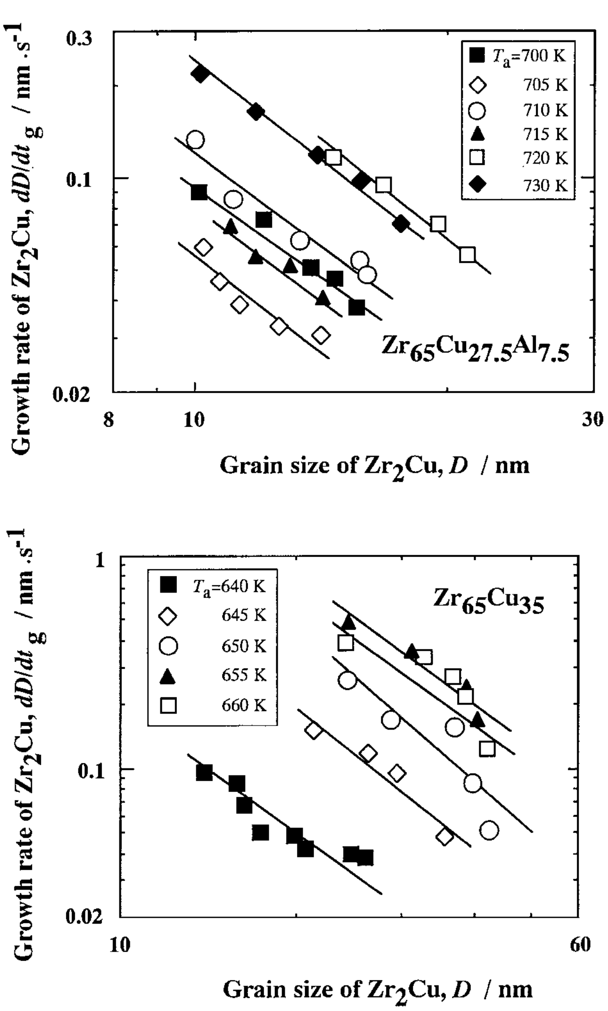

Figure 6 Logarithm of growth rate versus grain size for the $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ metallic glasses as a function of annealing temperature to obtain the kinetic order, N.

where k_0 is the frequency term, R is the gas constant, Q is the activation energy for grain growth and T_a is the absolute temperature of annealing. The grain size exponent of 3 indicates that the grain growth occurs in three dimensions [21, 22]. From the Equation 8, the rate constant, k is given by;

$$k = \frac{(D^3 - D_0^3)}{t_g} \tag{10}$$

indicating that k is obtained by the experimental data of D, D_0 and t_g for various annealing temperatures. Moreover, it is described from the Equations 8 and 9;

$$\ln\left[\frac{(D^3 - D_0^3)}{t_g}\right] - \ln k_0 = -\frac{Q}{RT_a}, \tag{11}$$

Therefore, the activation energy for grain growth can be calculated from the slope of the plot of $(D^3 - D_0^3)/t_g$ against $1/T_a$. Fig. 8 shows Arrhenius plots of $(D^3 - D_0^3)/t_g$ versus $1/T_a$ for $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$, where a straight line can be drawn through the data points and the slope of the curve gives $-Q/2.3R$ so that the activation energy for grain growth can be calculated to be

$$Q = 165 \pm 10\,\mathrm{kJmol^{-1}} \quad \text{for } Zr_{65}Cu_{27.5}Al_{7.5},$$
$$Q = 440 \pm 30\,\mathrm{kJmol^{-1}} \quad \text{for } Zr_{65}Cu_{35}.$$

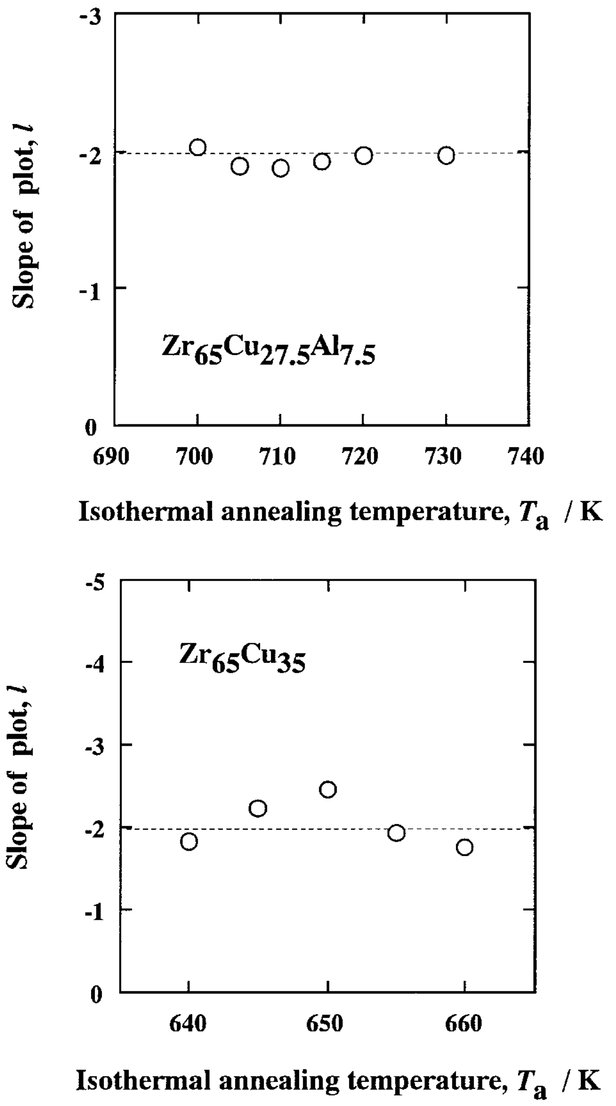

Figure 7 Change in the slope of Fig. 6 for the $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ metallic glasses.

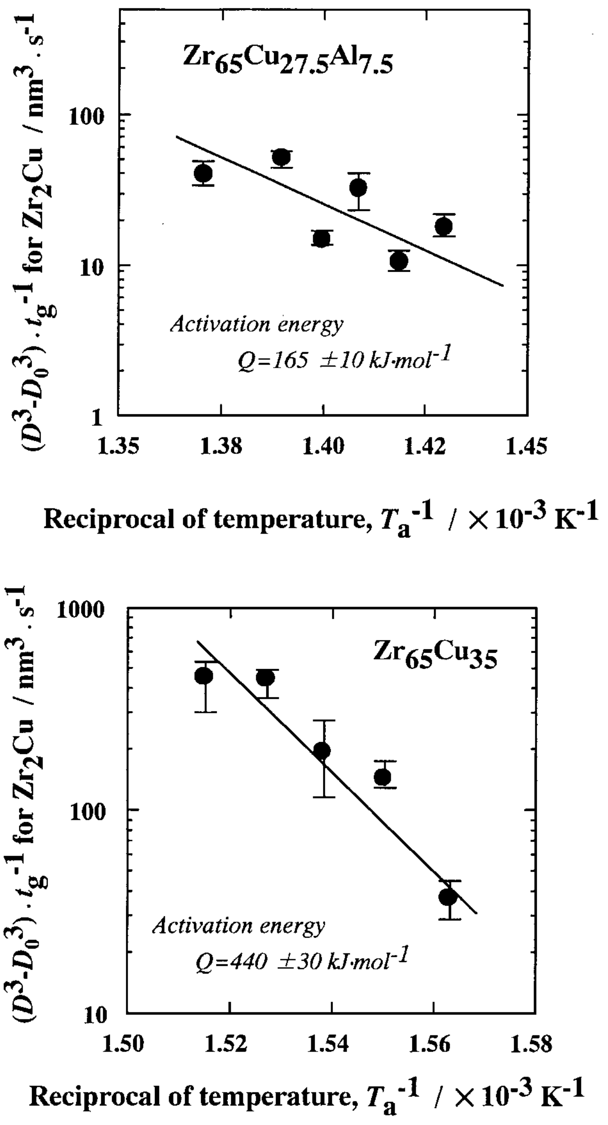

Figure 8 Arrhenius plots of $(D^3 - D_0^3)/t_g (= k)$ against $1/T_a$ for $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$. The slope gives the activation energy for grain growth as 165 ± 10 $kJmol^{-1}$ for $Zr_{65}Cu_{27.5}Al_{7.5}$ and 440 ± 30 $kJmol^{-1}$ for $Zr_{65}Cu_{35}$.

Table I summarizes the values of D_0, t_0, k and k_0, from which the average values of frequency terms, k_{0av} can be deduced to be

$$k_{0av} = (3.2 \pm 1.0) \times 10^{13}\,\mathrm{nm^3\,s^{-1}} \quad \text{for } Zr_{65}Cu_{27.5}Al_{7.5},$$

$$k_{0av} = (4.0 \pm 0.9) \times 10^{37}\,\mathrm{nm^3\,s^{-1}} \quad \text{for } Zr_{65}Cu_{35}.$$

The experimental error of k and k_0 is approximately ±20%. It is found that the activation energy for grain growth in $Zr_{65}Cu_{27.5}Al_{7.5}$ is lower than that in $Zr_{65}Cu_{35}$. The lower activation energy for $Zr_{65}Cu_{27.5}Al_{7.5}$ compared with that for $Zr_{65}Cu_{35}$ is also confirmed by Arrhenius plots of calculated growth rate at $t_g = 1$ s against a reciprocal of annealing temperature [15]. The difference in the activation energies is reflected the mechanism for grain growth. In the $Zr_{65}Cu_{27.5}Al_{7.5}$ glass, the grain growth seems to depend on the diffusion

TABLE I Values of D_0, t_0, the rate constant, k, frequency term, k_0 and the average of frequency terms, k_{0av} in Equation 9 at various annealing temperatures, T_a for $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$

Metallic glass	Temperature, T_a/K	D_0/nm	t_0/s	k/nm$^3 \cdot$ s^{-1}	k_0/nm$^3 \cdot$ s^{-1}	k_{0av}/nm$^3 \cdot$ s^{-1}
$Zr_{65}Cu_{27.5}Al_{7.5}$	700	7.7	270	16	3.3×10^{13}	$(3.2 \pm 1.0) \times 10^{13}$
	705	6.6	180	13	2.2×10^{13}	
	710	8.9	90	24	3.3×10^{13}	
	715	6.8	60	20	2.3×10^{13}	
	720	11.1	60	45	4.2×10^{13}	
	730	7.0	1	49	3.8×10^{13}	
$Zr_{65}Cu_{35}$	640	8.2	720	38	3.1×10^{37}	
	645	12.1	480	110	4.5×10^{37}	$(4.0 \pm 0.9) \times 10^{37}$
	650	8.8	240	200	4.5×10^{37}	
	655	9.5	120	360	4.4×10^{37}	
	660	12.5	60	530	3.5×10^{37}	

or rearrangement of Al, considering the growth rate in this study and the change in structure during crystallization in previous works [14, 15]. The lower activation energy of grain growth or crystallization corresponds to the rearrangement of only Al [23]. In contrast, as the crystallization depends on the rearrangement of both Zr and Cu, the higher activation energy is necessary for the crystallization and grain growth in the $Zr_{65}Cu_{35}$ glass. Especially, the higher activation energy might be consumed for the diffusion of large Zr atoms in the glass [24, 25]. Moreover, the order of magnitude as those for diffusion in the metallic glass during crystallization indicates the good correspondence to the activation energy. It is reported that the long-range rearrangement does not take place through the initial stage of crystallization by the addition of Al into Zr-Cu metallic glass [8, 12]. Therefore, the magnitude for diffusion at the initial stage of crystallization in the $Zr_{65}Cu_{27.5}Al_{7.5}$ glass is quite less than that in the $Zr_{65}Cu_{35}$ glass where the rapid precipitation and growth of the crystalline phase by diffusing many atoms at the same time take place with increasing annealing time.

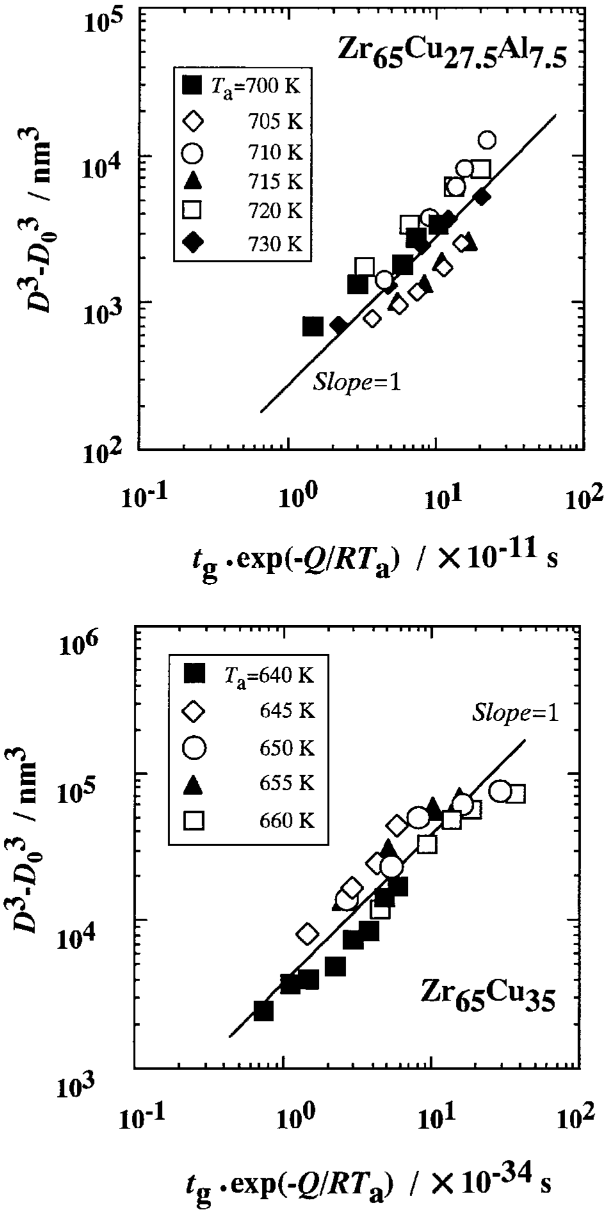

Figure 9 Relationship between $\ln(D^3 - D_0^3)$ and $\ln[t_g \exp(-Q/RT_a)]$ for $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$.

Therefore, Al seems to play a role in the suppression of the precipitation and growth of Zr_2Cu phase in the $Zr_{65}Cu_{27.5}Al_{7.5}$ glass. This investigation is also supported from the formation of ZrAl phase at the initial stage. The formation of ZrAl retards the precipitation and growth of Zr_2Cu phase resulting from restraining the diffusion of Cu and/or consuming the Zr with which Zr_2Cu should be formed. Thus, the reason for the formation of ZrAl at the initial crystallization stage is presumed to result from the difference in the heat of mixing among the constitutional elements discussed in previous work [14].

Finally, to verify the single kinetic law described by Equation 8, the grain growth data are rearranged in the relation between $\ln(D^3 - D_0^3)$ and $\ln[t_g \exp(-Q/RT_a)]$ by substituting the activation energy, grain size and annealing temperature in Fig. 9 for $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$. It is clearly seen that a single straight line with a slope of 1 can be drawn through the data points for both metallic glasses. This fact verifies that the single kinetic law prevails over data points obtained in the temperature ranges.

4. Conclusions

The grain growth kinetics in crystallization from a supercooled liquid region of the $Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{35}$ metallic glasses has been studied from isothermal annealing combined with X-ray line-broadening analysis. The results obtained are summarized as follows:

(1) The line-broadening of X-ray diffraction peak is attributed to only the change of grain size, resulting from the unchanged lattice spacing during the isothermal annealing and Hall's analysis for various diffraction peaks.

(2) The grain growth is controlled by a single kinetics with a thermal activation process of Arrhenius type, which is described by

$$D^3 - D_0^3 = k_0 t_g \exp\left(-\frac{Q}{RT_a}\right).$$

The average k_0 for all the temperatures is calculated as follows:

$$k_{0av} = (3.2 \pm 1.0) \times 10^{13}\ \mathrm{nm^3\,s^{-1}} \quad \text{for } Zr_{65}Cu_{27.5}Al_{7.5},$$

$$k_{0av} = (4.0 \pm 0.9) \times 10^{37}\ \mathrm{nm^3\,s^{-1}} \quad \text{for } Zr_{65}Cu_{35}.$$

This kinetics shows that the crystalline grain grows in three dimensions at the initial crystallization stage.

(3) The activation energy for the grain growth of Zr_2Cu is 165 ± 10 kJ mol^{-1} in $Zr_{65}Cu_{27.5}Al_{7.5}$ and 440 ± 30 kJ mol^{-1} in $Zr_{65}Cu_{35}$. The lower activation energy in the ternary glass is attributed to the mechanism of which the crystallization and grain growth are dominated by redistribution of only Al. However, the higher activation energy in the binary glass might be

consumed for the diffusion of the large Zr atom. It is concluded that the difference in the grain growth mechanisms is due to the strong chemical affinity between Al and Zr, which is an important factor of stabilizing the glassy state.

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