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Composition dependence of crystal growth and its time evolution in supercooled liquid of Zr–Al–Cu glassy metals

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Abstract

Crystal nucleation and its time evolution during isothermal annealing in supercooled liquid of glassy metals $Zr_{65}Al_{10}Cu_{25}$ ribbon, $Zr_{50}Al_{10}Cu_{40}$ ribbon, and $Zr_{50}Al_{10}Cu_{40}$ bulk are examined using a technique of differential thermal analysis. Time dependence of the fraction of crystallization in supercooled liquid at several temperatures is analyzed by the Johnson–Mehl–Avrami (JMA) formula. The Avrami exponents are 3.0 ± 0.2 for $Zr_{65}Al_{10}Cu_{25}$ ribbon, and 3.9 ± 0.4 for $Zr_{50}Al_{10}Cu_{40}$ ribbon and $Zr_{50}Al_{10}Cu_{40}$ bulk. Relation between grown crystals in the supercooled liquid and the Avrami exponent can be explained reasonably. Plots of the fraction of crystallized volume versus a scaled time normalized by the half time of full crystallization almost collapse on a single curve. This suggests that the crystal growth obeys a universal process. The temperature dependence of the half time is discussed using the Williams–Landel–Ferry function.

Keywords: Zr-based glassy metal; Supercooled liquid; Crystal growth; Avrami exponent; Scaling law; Diffusion-controlled process

1. Introduction

One of the outstanding features of glassy metals is the existence of supercooled liquid, which is in a little higher energy state than amorphous state below the glass transition temperature T_g. Since the supercooled liquid is a meta-stable state, a crystallization temperature T_x would finally coincide with T_g in quasi-static process. This trend has been shown experimentally by Kimura et al. [1]. The supercooled liquid appears as an intermediate meta-stable state with a finite lifetime appearing on the way of the final crystalline state. The irreversibility between the supercooled liquid state and the crystalline one is not the case for the first kind of phase transformation. This irreversibility arises from that the crystalline state is an intrinsic stable state with the lowest energy over the whole temperatures below the melting temperature T_m.

The first work discussing the isothermal crystal nucleation and growth in the supercooled liquid in glassy metals has been carried out for $Zr_{65}Cu_{27.5}Al_{7.5}$ ($T_g = 665$ K and $T_x \sim 740$ K) by Kawase et al. [2]. They estimated the crystallization rate $y(t)$ from differential scanning calorimetry (DSC) data and obtained increasing values with increase of temperature from 3.1 at 673 K to 3.7 at 723 K as the Avrami exponent N by the Johnson–Mehl–Avrami (JMA) plots.

On the other hand, the structure transformation in equilibrium state has been studied theoretically [3–7] and experimentally [8–13]. Most of the structure transformations in thermal equilibrium state do not change the mean chemical composition between the old phase and the new one. In many cases, the growth velocity of the new phase is controlled by a short-range diffusion of chemical elements and N is expected to be 3 for latent germ nuclei or 4 for constant nucleation rate of germ nuclei [7]. When the velocity of crystal growth is controlled by a long-range diffusion process such as a case that the chemical composition of the new phase differs from the old one, N is 1.5 for latent germ nuclei and 2.5 for constant nucleation for three-dimensional system [7]. When N can be obtained for crystal growth in supercooled liquid of glassy metals, this suggests a mechanism of crystal growth in supercooled liquid, if the same simplified assumptions are realized in these glassy metals.

Fukami et al. have investigated the nucleation of germ nuclei and its time evolution in supercooled liquid of $Zr_{55}Al_{10}Cu_{35-x}Ni_x$ ($x = 0$, 5) by differential thermal analysis (DTA) [14]. The values of N are different from the values

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obtained in Ref. [2]. The curves of $y(t)$ scaled by the half time of the completion time of crystallization almost collapsed on one universal curve for $Zr_{55}Al_{10}Cu_{30}Ni_5$ but this was not the case for $Zr_{55}Al_{10}Cu_{35}$. These contradictory results to both theoretical results and other experimental results may be caused from the different compositional ratio of the constitutional elements. On this standpoint, in this study the compositional dependence of the Avrami exponent and the scaling law for $y(t)$ etc. is examined.

In the present study, using glassy metals $Zr_{65}Al_{10}Cu_{25}$ ribbon, and $Zr_{50}Al_{10}Cu_{40}$ ribbon and bulk, the time dependence of isothermal exothermic heat energy is measured as a parameter of the non-equilibrium degree $\Delta = T - T_g$. The time-dependent data are analyzed using the Johnson–Mehl–Avrami formula, and the scaling with the half time of full crystallization and the exponent law for the characteristic time is derived. Using these results, the growth mechanism of crystals in supercooled liquid is discussed.

In Section 2, the experimental procedures are described. In Section 3, the experimental results are presented and in Section 4, analyses and discussion are given.

2. Experimental procedures

The ribbon samples were prepared by a technique of melt spinning. The bulky samples were prepared by a technique of melt casting. The bulk samples are a form of rectangular plate of about 2 mm in thickness.

Isothermal DTA was curried out at various temperatures between T_g and T_x. The fraction of crystallization at a time t after crystals start growing, $y(t)$, was determined as a ratio $A(t)/A(\infty)$, where $A(t)$ is the area under the exothermic peak up to time t and $A(\infty)$ is the total area. The areas were derived by measuring the ordinate at closely spaced values of t and using the Simpson type integration.

3. Experimental results

X-ray diffraction patterns of $Zr_{65}Al_{10}Cu_{25}$ ribbon and $Zr_{50}Al_{10}Cu_{40}$ ribbon and bulk are shown in Fig. 1. X-ray diffraction patterns are typical for the amorphous state. Similar X-ray patterns are observed for samples whose surfaces are shaved off by about 0.5 mm.

In order to determine T_g, DTA was carried out with increasing temperature at 40 °C/min. The results are shown in Fig. 2. From these data, T_g and T_x are determined. The results are summarized in Table 1. There is no clear difference of T_g and T_x between the ribbon and the bulk of $Zr_{50}Al_{10}Cu_{40}$.

Table 1
The characteristic temperatures for glassy metals used in the present study

Sample	Form	T_g (K)	T_x (K)	ΔT_x (K)
$Zr_{65}Al_{10}Cu_{25}$	Ribbon	645	734	89
$Zr_{50}Al_{10}Cu_{40}$	Ribbon	713	788	75
$Zr_{50}Al_{10}Cu_{40}$	Bulk	711	789	78

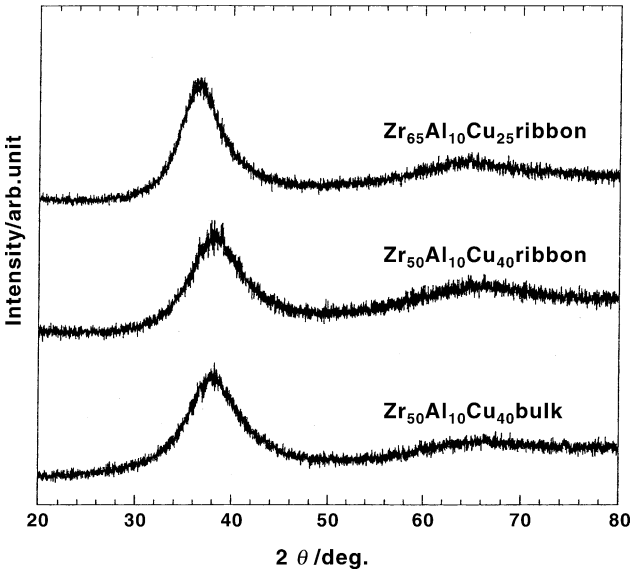

Fig. 1. X-ray diffraction pattern of three glassy metals.

Next, isothermal DTA for three samples was carried out at various temperatures in supercooled liquid region. The results are shown in Fig. 3. The peak height of DTA curves decreases, their width becomes wider and the raising time of DTA curve becomes longer with decreasing temperature, namely with decreasing Δ. This raising time can be considered as an incubation time of nucleation germs.

The crystallization ratio $y(t)$ was estimated from the curves shown in Fig. 3. The origin of time t is the raising point of DTA curves in Fig. 3. Fig. 4 shows the plots of $y(t)$ versus $\ln t$ for three samples. The sinusoidal form of the curves is very similar regardless of the set temperature.

After isothermal DTA, the X-ray analysis was carried out for these samples. The results are shown in Fig. 5. Several diffraction peaks of Zr_2Cu are observed for $Zr_{65}Al_{10}Cu_{25}$. For

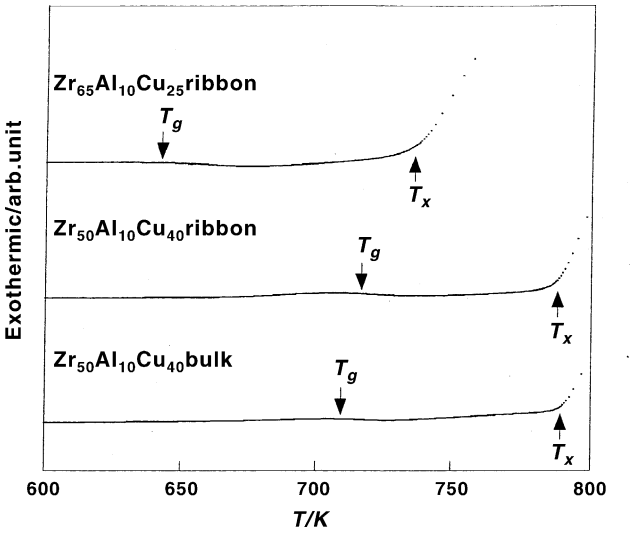

Fig. 2. Data of differential thermal analysis (DTA) for three samples. T_g and T_x are the glass transition and crystallization temperatures, respectively.