Crystal Growth in the Bulk-Metallic-Glass Zr-based Alloys by Using the DC + AC Levitation Method

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Abstract. A levitation method using the alternating and the static magnetic fields suppresses convection in a levitated melt and consequently enables us to measure crystal growth velocity as low as 0.5 mm/s in the undercooled melt. Crystal growth velocities of the constituent phases in the bulk-glass-forming Zr-Ni-Al and Zr-Cu-Al alloys were measured. The growth velocities at the bulk-glass-forming compositions in the Zr-Ni-Al and the Zr-Cu-Al alloys were as low as 1 mm/s even if the undercooling exceeded 100 K. The interface kinetics and the solute transport of rejected elements resulted in the low growth velocities. The BMG formation in the metal mould casting can be explained by considering the competition between the crystal growth and the glass transition.

1. Introduction

High glass forming ability (GFA) has been recognized for Zr-based alloys [1,2,3,4]. It has been also reported that the local atomic order, such as the icosahedral order, was closely related to the high GFA [4-6]. Formation of glass phase is usually explained by considering suppression of nucleation. On the other hand, GFA can be also explained by considering growth of crystalline phases in the undercooled melt. For example, rapid melting by laser irradiation causes rapid solidification due to heat extraction into inside and the glass phase can be formed in the surface region. The result indicates that the glass phase can be formed by suppressing the crystal growth. However, crystal growth velocity in glass forming alloys has not sufficiently been examined, comparing to the critical cooling rate [7]. In addition, an interesting solidification behavior was reported in the Zr-Cu-Al alloy [8]. Thus, it is of interest to know solidification manner in the glass forming alloys and the formation of glass phase by suppressing the crystal growth.

Containerless processes are useful methods to produce undercooling to examine solidification from the undercooled melt. Since heterogeneous nucleation on crucible walls and contamination from crucibles can be avoided, the highly undercooled melts can be obtained by the containerless processes. In the conventional electromagnetic levitation method, forced convection and oscillations due to the surface tension always occur in the levitated melt, because the electromagnetic force causes both the lift force through the magnetic pressure and the stirring force. The forced convection strongly disturbs solute diffusion around the growing crystals and consequently changes the growth morphology.
Therefore, it was impossible to observe solidification phenomena in which growth velocities of crystalline phases are relatively low without the disturbance.

Recently, a new electromagnetic levitation method using the alternating and the static magnetic fields has been developed [9]. The superimposition of the static magnetic field on the levitated melt suppresses the oscillation and the convection agitated by the alternating magnetic field. The typical intensity to suppress the convection is 0.5T. Thus, the static levitation by using the simultaneous imposition of the static magnetic field enables to measure the low crystal velocities in the undercooled melt. The preliminary experiments were performed in the Zr-Ni-Al and the Zr-Cu-Al alloys [7, 10, 11].

This paper presents crystal growth velocities in the bulk-metallic-glass-forming Zr-Ni-Al and Zr-Cu-Al alloys. On the basis of our experimental results, the nucleation and the solidification of the bulk-glass-forming alloys were characterized.

2. Experiments

An electromagnetic levitation method using the alternating and the static magnetic fields [9] was used to examine nucleation and crystal growth, as shown in Fig.1. An RF generator (200kHz, 20kW) was connected to a levitation coil. A cryogen-free superconducting magnet imposed a static magnetic field up to 1T. Growth of crystalline phases in the levitated melt was observed by a high speed CCD camera (10,000fps max). Growth velocity was estimated from the recorded images. Temperature of a levitated melt was measured by a two-color pyrometer. Temperature measured by the two-color pyrometer was calibrated, so that the temperature measured by the pyrometer coincided with the temperature measured by a thermocouple inserted into the melt.

![Figure 1. Setup of the levitation apparatus that uses the alternating and the static magnetic fields. The alternating magnetic field is applied by the coil, inducing the lift force. The static magnetic field is applied by the superconducting magnet, suppressing the convection in the melt. Crystal growth is observed by a high-speed CCD camera.](image)

Typical diameter and mass of a levitated specimen were 5 mm and 0.8-1.0 g, respectively. Melts were initially levitated in a pure Ar atmosphere. Overheating of a melt was approximately 200K. The levitated melt were cooled by He-5%H₂ or He gas. Cooling rate of the melt ranged from 20 K/s to 100 K/s. In the recorded images, crystalline phases were detected due to difference in emissivity. Growth rate of crystalline phase was evaluated from the sequential images. A static magnetic field of 1.5T or 0.6T was imposed to measure crystal growth velocities.

Investigated compositions were 60at%Zr -25at%Ni -15at%Al, 66.7at%Zr -33.3at%Ni and 66.5at%Zr -33.2.at%Ni -0.3at%Al. The glass phase is easily formed at 60at%Zr -25at%Ni -15at%Al. Effect of Al addition into Zr-Ni alloys on growth velocity of the Zr₂Ni compound was also examined at a composition of 66.5at%Zr -33.2.at%Ni -0.3at%Al. For comparison, Zr-Cu-Al alloy with a composition of 50at%Zr -40at%Cu -10at%Al was also examined.

3. Results and discussion

3.1. Zr-Ni-Al alloys

Figure 2 shows the crystal growth velocities of the crystalline phases in the Zr-Ni-Al alloys. The growth velocity of Zr₂Ni compound in the binary alloys ranged from 10 mm/s to 100 mm/s in the
undercooling range of 0-40 K. In the case of Ni, the growth velocity monotonically increased with increasing undercooling and the growth velocity was estimated to be of the order of $10^2$ m/s in an undercooling of 15K [12,13]. In the case of Ni-B dilute alloys, the growth velocity was still of the order of $10^2$ m/s, although the addition of B reduced the velocity [12]. Thus, the growth velocity of the Zr$_2$Ni compound was relatively low, comparing to the growth velocities of conventional metallic alloys. The addition of Al (0.3at%) into the Zr-Ni alloy significantly reduced the growth velocities. The growth velocity became less than 10 mm/s even at the undercooling of 80K. Furthermore, the growth velocity became less than 1 mm/s even at a undercooling exceeding 100K in the Zr$_{50}$Ni$_{25}$Al$_{15}$ alloy (glass forming composition). The result showed that the growth velocity at the BMG forming composition became as low as 1 mm/s.

Figure 2. Growth velocity of the crystalline phases in Zr-Ni-Al system. The undercooling was defined as difference between the liquidus temperature and the melt temperature.

![Figure 2](image)

Figure 3. Typical cooling curves of the bulk-metallic-glass forming Zr$_{50}$Cu$_{40}$Al$_{10}$ alloy. The liquidus temperature is indicated by the dashed line.

![Figure 3](image)

3.2. Zr-Cu-Al alloys

Figure 3 shows a typical cooling curve of the Zr$_{50}$Cu$_{40}$Al$_{10}$ alloy. The dashed line indicates the liquidus temperature. Changes of cooling rate corresponded to nucleation events. The recalescence was not clearly observed for the Zr$_{50}$Cu$_{40}$Al$_{10}$ alloy. Namely, the heat release due to crystal growth was not sufficient to increase temperature of melt up to the liquidus temperature. According to the microstructure observation, $\tau$3, ZrCu with B2 structure and Zr$_2$Cu were observed in the solidified structure. However, the primary phase was not identified from the solidified structure. The nucleation undercooling ranged from 50K to 120K and did not depend on cooling rate in the present experimental setup (cooling rate: 20K- 200K/s). The growth velocity did not exceed 1 mm/s even at a undercooling of 100K.
3.3. Low growth velocity and glass forming ability

The formation of the glass phase has been explained by considering the nucleation event. On the other hand, the formation can also be considered in terms of the crystal growth. If the glass phase is treated like a crystalline phase, manner of solidification at the glass forming compositions can be regarded as being a competition between the growth of the crystalline phases and the formation of the glass phase [7]. The glass transition temperature (approximately 973 K) corresponds to the melting point; the solute partition coefficient is unity (no solute rejection); the latent heat is extremely small. Although the lower melting point of the glass phase is a disadvantage for growth, the glass phase is superior to the crystalline phases in terms of solute redistribution and latent heat release at the solidifying front. When the moving velocity of the isothermal plane at the glass transition temperature is sufficiently higher than the crystal growth velocities, the isothermal plane, which is regarded as the growing interface of the glass phase, overtakes the advancing front of the crystalline phase and consequently the glass phase is formed ahead of the crystals.

In the metal mold casting (i.e. diameter: 10mm), the typical moving velocity of the isothermal plane in the Zr-Ni-Al alloys is in the order of 10 mm/s. The crystal growth velocities observed in the glass forming compositions of the Zr-Ni-Al and the Zr-Cu-Al alloys are smaller than the estimated moving velocity. Thus, the crystals stop growing even if the nucleation events take place at the boundary between the melt and the mold. The low growth velocities (less than 1 mm/s) in the Zr-Ni-Al and the Zr-Cu-Al alloys are beneficial for fabricating the BMG with rather large size.

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