Analysis of solidification processes in amorphous Zr-Cu-Al alloys

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Abstract. The relationship between metallic glass properties and the cooling behavior of Zr₆₅Cu₂₇.₅Al₇.₅, Zr₅₈Cu₃₃Al₉ and Zr₅₀Cu₃₉.₃Al₁₀.₇ alloys was investigated using an electromagnetic levitation heater combined with a spin coater style quenching system. The quenching process was monitored by the high-speed camera and the thermospot sensors. About forty millimeters amorphous disks were obtained. The maximum temperatures and the maximum cooling rates at the center of the disk were 500°C and 30% higher than the values at the 15mm outer from the center position. Cooling process affected the glass-forming abilities. The temperature differences between the glass transition and crystallization onset temperatures (∆Tₓ) of the center position were 10 to 20% higher than those in the outer.

1. Introduction
Zr-Cu-Al alloys are known as Zr-based bulk metallic glasses (BMGs). The properties of BMGs are expected to be utilized in various industrial items. Recent subjects are summarized elsewhere [1, 2]. In industrial applications, the fabrication method must ensure high reproducibility. Casting or melt spinning are convenient ways to fabricate BMGs. BMGs have been fabricated by casting, splat cooling or single-roller quenching. Unfortunately, it is difficult to directly observe the solidification in these processes. Solidification or cooling behavior is a key factor in producing BMG materials, but the glass properties in the solidification process have seldom been evaluated. BMGs are attractive materials, but there are still some problems, such as the relation between structural relaxation and plastic deformation. Clarifying the relationship between the solidification process and the glass-forming properties will help to solve these problems and improve reproducibility for industrial use. This work focuses on Zr-Cu-Al alloy. This is a typical BMG material, and the composition range of BMG forming has been studied [3]. Three compositions, Zr₆₅Cu₂₇.₅Al₇.₅, Zr₅₈Cu₃₃Al₉ and Zr₅₀Cu₃₉.₃Al₁₀.₇, were prepared. The compositions are elements of the pseudo-binary system of Zr-Cu₁₁Al₃ alloys. The sample is heated by an electromagnetic levitation, which is one kind of containerless processing. In producing BMG materials, containerless processing has the merit of not requiring a sample holder or nozzle in the heating. A few approaches for utilizing levitation for producing BMG materials take advantage of this merit [4, 5]. The method is utilized to produce metastable materials [6] and to measure the surface tension of melt materials [7].
The melt sample is solidified by a spin-coater quenching system, which can directly observe the solidification process [8]. The relationship between the cooling process and BMG properties is discussed.

2. Experiment Procedure

$Zr_{58}Cu_{33}Al_{9}$, $Zr_{50}Cu_{39.3}Al_{10.7}$ alloy ingots were prepared by arc melting a mixture of 3N grade Zr and 4N grade Cu and Al reagents (Rare Metallic Co., Ltd.). The alloy ingots were remelted by an electromagnetic levitation system (JEOL JTR-10). The induction coil in the levitation system is installed around a quartz glass tube containing an Ar gas atmosphere. The induction coil is heated by a 400kHz electric current. The samples weighed 0.9 to 1.5g. When the heating starts, the sample is also levitated. After 40 seconds of heating, the induction coil is turned off and the melt sample drops onto the spin coater quenching system. The sample drops 370mm to the disk, and the final drop speed is 600mm/s. The cooling disk is 50mm in diameter and rotates at 7200rpm. Three types of cooling disks, Cu, brass and stainless steel (SUS304), are used. The disks had thermal conductivities of 402W/mK for Cu, 119W/mK for brass, and 15W/mK for stainless steel. The sample temperatures were measured by thermospot sensors (TSS, Japan Sensor Co., Ltd., FTZ-6) over a range of 400 to 2000°C. The sample temperature was measured at three points: the levitation point (the heating temperature), the cooling disk center (the cooling temperature when the droplet first contacts the disk), and 15mm from the center (the cooling temperature of the expanded droplet). The center point corresponded to the axis of the rotating cooling disk. The cooling process on the disk is also observed by a high-speed camera (MEMRECAM ci) at a frame rate of 2000 pixels per second. A single trigger initiates the high-speed camera and the TSS measurements. The products were analyzed by X-ray diffraction (XRD, Mac Sci. MXP-3) and differential scanning calorimetry (DSC, Rigaku Thermo Plus DSC 8270).

3 Results and Discussion

The melt sample was produced by the electromagnetic levitation heater. The sample temperature was monitored by TSS. The sample was rapidly heated until the temperature saturated at 1700°C at around 30 seconds. After then, the heating was terminated, and the sample was dropped. The cooling behavior was analyzed by in-situ observation with the high-speed camera and two-point TSS measurements on the cooling disk. Figures 1 to 3 depict the typical results for the $Zr_{50}Cu_{39.3}Al_{10.7}$ alloy cooled by a brass disk. Figure 1 presents the cooling behavior at the center and outer positions on the brass cooling disk. The spotlights on the cooling disk in Fig. 1 indicate the present measurement points. TSS temperatures increased before the droplet reached the disk. The cooling disk had a mirror surface, so TSS measurements detected the reflected droplet image. The droplet was 12mm in diameter, and the expansion time on the disk was 20ms. The cooling temperature in the center was raised to 1700°C and held for 10ms. The temperature was then decreased at a rate of -12000°C/s. At 0.315s, the cooling rate was increased to -50000°C/s. The cooling temperature at the outer position was raised to 1200°C and then decreased at -12000°C/s. At 0.328s, the cooling rate was increased to -33000°C/s. The cooling process was also observed by high-speed camera, and

![Figure 1](image_url)
the series of images acquired is presented in Fig. 2. The time scale corresponds to that in Fig. 1. When the droplet touched the cooling disk, it expanded to the disk shape in 20 ms. The range corresponds to the peak temperature of the center position in Fig. 1. The sample expanded to the disk shape in 0.31 s. After then, the bright high-temperature area was removed from outer to center.

The products at the center and outer, which were the measurement positions in Fig. 1, were analyzed XRD. The XRD results confirmed that the sample did not contain crystal phases. The temperature differences (ΔTx) between the glass transition temperature (Tg) and the crystallization onset temperature (Tx) were determined by DSC measurement.

Figure 3 shows the DSC curve of the products at the center and the outer positions. The measurements were made in vacuum, and the heating rate was 10 °C/min. The Tg and Tx at the center were 353.1 °C and 447.4 °C, and the outer were 370.9 °C and 447.0 °C. Therefore, ΔTx at the center was 92.4 °C, and outer was 82.3 °C. High temperature and high cooling rate are advantageous when producing metallic glass material with a wide range of ΔTx.

To clarify the relationship between the solidification process and the glass-forming properties, the same experiments were conducted with other compounds and cooling disks; the results are summarized in Table 1. All experiments yielded disk style products, and there were no obvious differences in the forms of these products. The largest sample was about 50 mm in diameter. The melt viscosity increased with decreasing melt temperature [9]. The limitation meant that there was a transition point of the melt sample from expansion to cohesion of small droplets due to increased viscosity.

The Tg, Tx, and ΔTx (∆Tx=Tx-Tg) are also summarized in Table 1. The ΔTx values of the outer position were 10 to 20% lower than those in the center. The reported ΔTx value for Zr65Cu35Al9 was 90 °C, that of Zr58Cu33Al9 was 80 °C, and that of Zr50Cu39.3Al10.7 was 70 °C [3]. The ΔTx values at the outer positions of samples Zr58Cu33Al9 and Zr50Cu39.3Al10.7 were similar. The experiment conditions at the outer positions were similar to those of the single-roller quenching process. However, the experiment conditions at the center positions...
differed from the reported ones. The maximum temperatures were around 1800°C, which is almost 500°C above the values at the outer positions. Due to the use of a silica glass nozzle, the single-roller quenching process or other popular rapid-cooling processes were difficult to apply to the temperature range. However, high temperature increased the viscosity, which subsequently improved cooling on the cooling disk.

Thermal conductivity is an important factor in cooling, but the wetting between the melt sample and stainless steel disk should also be considered. We did not consider the effects of wetting in this study. However, some studies have investigated the molding melt sample on silicon wafers [10]. The present experiments revealed the tendency for the wetting of BMG materials for Cu and brass to be better than that for stainless steel. Wetting will be the subject of our next study.

### Table 1
The experimental results and the glass forming properties of Zr-Cu-Al Alloys

| Composition | Cooling Disk | Start. Weight | Recov. rate | Diameter | Position | $T_{\text{max}}$ | Cooling rate | XRD | $T_g$ | $T_x$ | $\Delta T_x$ |
|-------------|--------------|---------------|-------------|----------|----------|-----------------|--------------|------|------|------|---------|
| Zr50Cu35Al15 | Cu 1.2240 76.48 42 Center 1700 49000 amo. 371.5 460.7 89.2 | 1.3178 74.95 45 Center 1800 50000 amo. 372.5 460.4 87.9 | Stainless 1.3178 47.24 42 Center 1700 46000 amo.+cryst. 371.6 460.6 89.0 | | | |
| Zr50Cu35Al15 | Cu 1.0040 66.78 35 Center 1700 50000 amo. 346.1 445.1 99.0 | 1.2449 82.91 49 Center 1700 50000 amo. 353.1 447.4 94.3 | Stainless 1.0998 48.54 42 Center 1700 55000 amo. 348.3 444.0 92.7 | | | |
| Zr50Cu35Al15 | Cu 1.3480 72.68 38 Center 1900 48000 amo. 334.2 418.9 84.7 | 0.9965 51.87 31 Center 1750 49000 amo. 338.0 419.4 81.4 | Stainless 1.1760 31.97 31 Center 1750 38000 amo.+cryst. 331.5 421.1 89.6 | | | |

4. Conclusion
In situ observation of the solidification process using a spin coater style quenching system indicated that the cooling process strongly affected the BMG properties. The Zr-Cu-Al alloys solidified from 1700°C had about 20% better $\Delta T_x$ values than alloys solidified from 1250°C because of the high cooling rate. When the amount of Zr in the composition increased, the glass transition temperature ($T_g$) and the crystallization onset temperature ($T_x$) decreased, although the temperature difference between them, $\Delta T_x$, improved by 10%, which is half scale of the improvement in the solidification process.

Suitable cooling conditions improved the glass-forming properties without changing the composition.

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