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Melting and phase-separation of lead borate glasses in low gravity drop shaft

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Abstract

A drop shaft experiment was conducted to melt and solidify a glass of $3.5PbO–96.5B_2O_3$ (mol%) composition adhered to a small platinum heating coil (2–3 mm i.d., 5–6 mm long) at the Japan Microgravity Center (JAMIC). The temperature of glass melt recorded during the drop experiment indicates that the phase-separation of this glass mainly happened during the high gravity period of the experiment. A similar experiment was conducted on the ground to explore the effect of gravity level on the melting and phase-separation of lead borate glass. The homogeneity of different samples was compared through EDS analysis and the microstructure of the samples were observed by SEM. The lead borate glasses separated into two different glass phases, the separated phase (Pb-rich phase) and the continuous phase (B-rich phase), regardless of the gravity level the phase-separation happened. The size of separated Pb-rich phase in the top of sample from drop shaft experiment is much smaller than that in the bottom of sample, while the sizes of separated Pb-rich phase are almost the same in different locations in the ground sample. The homogeneity of the drop shaft sample is much worse than that of ground sample.

Keywords: Lead–borate glass; Drop shaft experiment; Phase-separation

1. Introduction

The drastic reduction in hydrostatic pressure, sedimentation, buoyancy or gravity-driven convective flows in a low gravity environment have consequences on virtually all processes involving fluids, such as the solidification of melts [1–3]. Many weak, physical forces, such as surface tension and diffusion, which generally remain masked by gravity driven convection at 1*g* become prominent and measurable in low gravity, thereby, provide the opportunity to identify their role in materials processing.

The melting and solidification of glasses in low gravity is attracting the interest of more and more glass researcher [4,5] and the phase-separation of glass under microgravity is also an interesting field of study. Because of the big difference in density of two separated phase of $PbO–B_2O_3$ glass after phase-separation, glasses in the $PbO–B_2O_3$ system are often chosen to study the phase-separation of glass under microgravity [6–8].

In this study, the melting and phase-separation of lead borate glasses during drop shaft experiments was explored and compare with that of samples from the ground experiment. The composition homogeneity and microstructure of the drop shaft sample and ground sample are investigated.

2. Experiment

2.1. Drop apparatus

A drop shaft experiment was conducted at the Japan Microgravity Center (JAMIC) whose drop shaft is 710 m in height. The free falling distance of the drop capsule containing experimental package is 490 m, which is in low gravity period of ~10 s. The deceleration distance is 220 m, which is in high gravity period. The value of gravity was $<2 \times 10^{-3}g$ ($\pm 5 \times 10^{-4}g$) during 10 s of low gravity time and was $\sim 9g$ during capsule deceleration.

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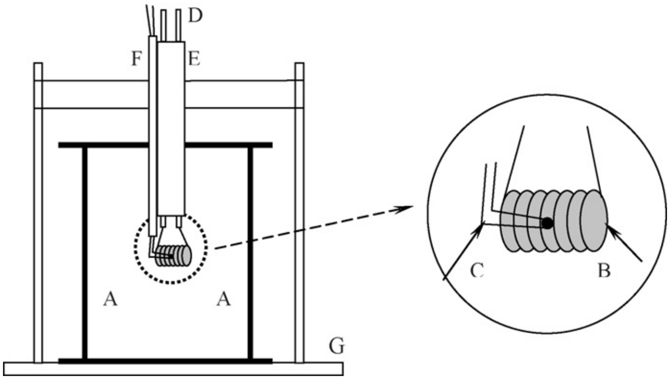

Fig. 1. Schematic of the apparatus used for experiments in the JAMIC drop shaft. (A) Glass box; (B) platinum heating coil holding the glass sample; (C) Pt–Pt/13% Rh thermocouple; (D) copper wire leads; (E) refractory tube holding heating coil; (F) refractory tube holding thermocouple; (G) main frame.

The apparatus used for the drop experiments is shown schematically in Fig. 1, which consists of a glass box (A), a platinum heating coil (B) holding the glass sample and a Platinum–13% Rhodium thermocouple (C). The heating coil, ~5 mm long and 3 mm internal diameter, was prepared using 0.3 mm diameter platinum wire (~15 turns). The two ends of the heating coil were attached to thick (~2 mm diameter) copper wire leads (D), which were connected to power supply after taking them through a two-hole refractory tube (E). The purpose of using low resistance (thick) copper leads is to minimize the heat loss and to obtain a high temperature (at the coil) with a relatively low power input.

The refractory tube (F) holding the thermocouple was glued to the refractory tube (E) holding the heating coil after positioning the thermocouple tip approximately at the center of the coil. An appropriate amount of glass was fused to the coil by passing a small amount of current through the coil that is just sufficient to melt the glass. The experiments were conducted in air at normal atmospheric pressure.

During the drop shaft experiment, the voltage and current of the heating coil were recorded and the temperatures of the melts in different time were also collected.

2.2. Preparation of glass

Lead oxide (99.9%, Aldrich) and borate acid (99%, Fisher) were used as the starting materials. The glass was prepared by melting mixture of weighed batch material in a platinum crucible with a muffle furnace at 1100 °C for 1 h and quenching the melt between two pieces of carbon steel plates. In order to ensure homogeneity of the glass, the quenched melt was ground into fine powders, well mixed, and sintered at 600 °C for 2 h. The sintered bulk was then crushed into small pieces for use in the heating coil for drop experiments.

2.3. Analysis of the samples

The compositions of samples were analyzed using energy dispersive X-ray analysis (EDAX). The microstructures of samples were observed using scanning electron microscope (SEM).

3. Results and discussion

The voltage and current profile of the drop shaft experiment are shown in Fig. 2 as a function of time, and the temperature profile for the drop shaft experiment is shown in Fig. 3 along with the gravity value achieved in this experiment.

The power was turned off as soon as the drop capsule began to drop, as shown in Fig. 2. The temperature of the melt at the end of the low gravity time was about 710 °C, and the sample was still in the liquid state when the capsule started decelerating. It is known [9] that the immiscible temperature of the 3.5PbO–96.5B_2O_3 is ~740 °C. for this melt was attained at about 1.3 s before the end of low gravity time, see Fig. 3. This means that phase-separation of the melt in low gravity occurred for only 1.3 s in low gravity (at the very end of the low gravity duration), which, however, continued in high gravity. Thus, any phase-separation occurred in this sample should be attributed primarily to the effect of high gravity (8–10*g*).

To explore the effect of gravity condition on the phase-separation of the lead borate glass, a ground drop experiment with the similar heating program to that of drop shaft

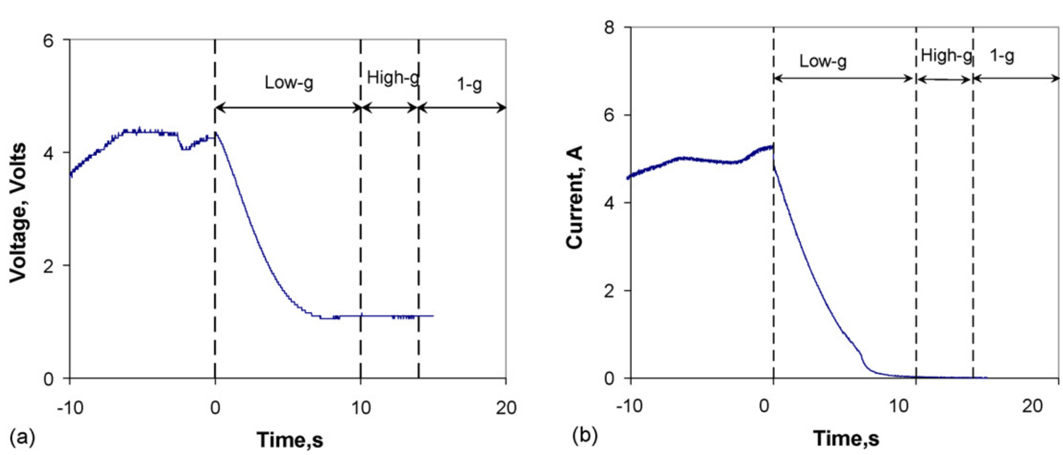

Fig. 2. The voltage (a) and current (b) to the heating coil as a function of time in JAMIC drop shaft experiments.

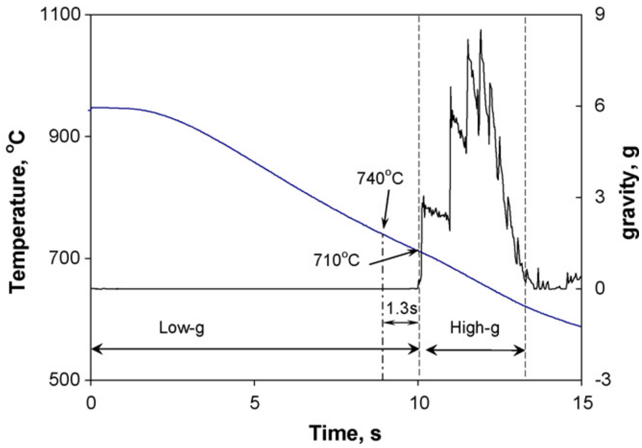

Fig. 3. Temperature of the melt and gravity value for drop shaft experiment.

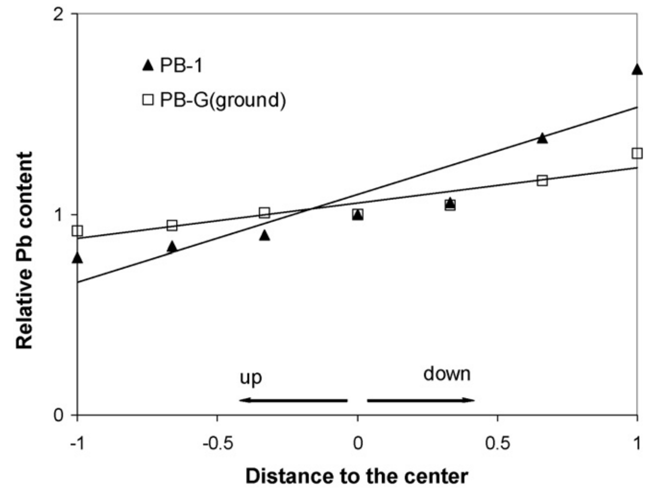

Fig. 4. Relative lead content in the cross-section along the gravity direction for different samples.

experiment was conducted. Both the ground sample and drop shaft experiment are not transparent and the X-ray diffraction analysis indicate that there is no crystalline phase exists in the sample and the main phase of the sample is glass. Therefore, it is believed that the samples both phase-separated into two glassy phases, one lead-rich and the other borate-rich.

Fig. 4 gives the lead concentrations in different locations along the gravity direction of the cross-section of samples as a function of the relative distance of each chosen position to the cross-section center. The relative lead concentrations increase from the top to the bottom of the cross-section for both the samples. It is known that the composition of glass melt before phase-separation is homogenous. Two immiscible liquid phases, continuous borate-rich liquid with low density and separated lead-rich droplets with high density will appear after phase-separation. When the viscosity is low enough for the liquids to move, the borate-rich liquid will move upward while the lead-rich droplets downward due to the effect of gravity, resulting in the heterogeneity of composition alone the vertical direction of samples.

It can be found that composition difference between top and bottom of the drop shaft sample is much higher than that of ground experiment, which is believed to be close related to the gravity condition the samples melted and phase-separated. For

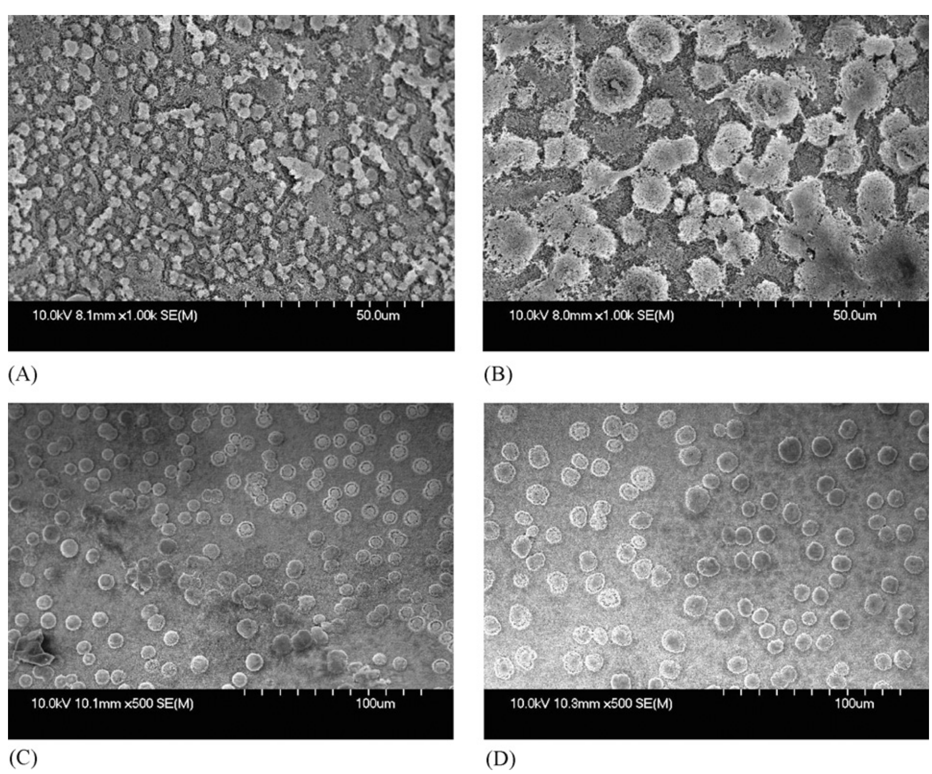

Fig. 5. SEM picture at different locations of the drop shaft and ground sample. (A) Top of drop shaft sample; (B) bottom of drop shaft sample; (C) top of ground sample; (D) bottom of ground sample.

the drop shaft sample, the liquids after phase-separation will move easier and faster under high gravity than those under normal gravity, causing more lead-rich droplet accumulate in the bottom and less lead-rich droplet in the top.

The SEM pictures at top and bottom of the drop shaft sample and ground sample are shown in Fig. 5. All the pictures are taken at the same magnification. As anticipated, the microstructure of the sample clearly contains two phases, one phase (nearly circular region) dispersed into a continuous matrix phase. It is believed that the circular regions are lead-rich phase and the continuous matrix is the borate-rich phase.

For the drop shaft sample, the microstructures of the top and bottom locations are considerably different. The size of the lead-rich phase is much larger at the bottom than that at the top location of the sample. As discussed above, there are more lead–borate droplets gather in the bottom of sample than those in the top, the droplets in the bottom are much easier to collision, combination and grow into large droplets than those in the top.

Unlike the drop shaft sample, the size of the lead-rich phases at a bottom location of the ground sample is only a little larger than that at a top location of the sample.

4. Conclusions

The recorded temperature of melt during drop shaft experiment indicates that the drop shaft sample phase-separated mainly during the high gravity period. Both the drop shaft sample and ground sample formed two glass phases after phase-separation: one is a continuous borate-rich phase and the other is a separated lead-rich phase. The density difference between the two phases results in the reciprocal movements of them due to the effect of gravity. High gravity is the main reason for the evident heterogeneity of composition along the gravity direction and the differences in size of the separated phase in the top and bottom of the drop shaft sample.

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