Thermal Diffusivity of Zr-Based Bulk Glass Alloys in the Liquid State

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Thermal diffusivity of three alloys of Zr55Al10Ni5Cu30, Zr60Al15Ni25, and Zr60Al7.5Cu27.5 has been measured in the liquid state with a laser flash technique. The thermal diffusivity values of three Zr-based alloys in the liquid state are summarized in the linear equations with positive temperature dependency. The lower the thermal diffusivity values of Zr-based alloys at liquidus temperature, the lower the critical cooling rate to produce metallic glass phase becomes. The measured thermal diffusivity was compared with the value for Pd-based metallic glass. The results indicate that critical cooling rate to obtain metallic glass phase could be an increasing function of thermal diffusivity for each alloy system.

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1. Introduction

Zr-based glassy alloys with particular composition, such as Zr55Al10Ni5Cu30, are well known to exhibit glass transition with a wide supercooled liquid region.1 The extremely high level of thermal stability of supercooled liquid state enables us to produce bulk metallic glass with a shape on the order of several centimeters in thickness. These bulk metallic samples allow us to investigate their thermal properties and electrical resistivity. Thermal properties of these alloys are of importance to estimate a temperature profile in a mold. The thermal diffusivity values of Pd-Cu-Ni-P system in the liquid state have been recently reported,2 and the results indicate that the Pd40Cu30Ni10P20 alloy shows the lowest value of thermal diffusivity (and thermal conductivity) among the measured alloys. It is also suggested that the critical cooling rate to obtain metallic glass phase of this alloy system could be a function of thermal diffusivity. However, this Pd-based alloy contains non-metallic element of phosphorus. Then, some further experimental results for alloys without non-metallic element are required. Since a limited number of alloys are known to produce a bulk shape of glass, we need the precise values of thermal diffusivity or thermal conductivity of such particular alloys. The purpose of this work is to present the thermal diffusivity values of three alloys for Zr-Al-Ni-Cu system, which consists of metallic elements only, in the liquid state. It was also be worthy of note that the Zr55Al10Ni5Cu30 alloy shows the wide supercooled liquid region of 140 K. The thermal diffusivity of these Zr-based alloys was compared with the Pd-based alloy case and the glass-forming ability of these alloys is also discussed.

2. Experimental Procedure

Three alloys of Zr55Al10Ni5Cu30, Zr60Al15Ni25 and Zr60Al7.5Cu27.5 were selected to determine the thermal diffusivity values. A Critical cooling rate of the Zr55Al10Ni5Cu30 alloy is about 10 K/s which is the lowest value among the three alloys. The mixture of pure Zr, Al, Cu and Ni were melted and cast into the mold under argon atmosphere. The as-cast sample of Zr55Al10Ni5Cu30 alloy was obtained with a shape of 50 × 20 × 2.2 mm3, and in the glass state. On the other hand, the as-cast samples of Zr60Al15Ni25 and Zr60Al7.5Cu27.5 were found to be crystallized in the crystallized state. The disk shape with a diameter of 10 mm and a thickness of 1 mm was machined from these bulk materials. This disk shape sample was contained in a sample holder, which is consisted of two quartz plates and a quartz tube with a graphite fixture. In the case of measurement for thermal diffusivity of Pd-based alloys, alumina plates with alumina tube were used as a sample container. It may be suggested that alumina is not suitable as the container for Zr-based alloys because the alloy samples containing Zr wet the alumina very well and liquid alloys penetrate through the thin gap between the plates and tube. The thermal diffusivity measurements were made in liquid state by a laser flash technique and the details are given elsewhere.

Temperature increase at the bottom surface of the sample was measured through the lower quartz plate by using an InSb infrared detector. The energy provided by pulse laser heating on the surface of the sample induces temperature gradient across the liquid sample. The convection due to change of density in the liquid sample is suppressed under this experimental condition because the temperature gradient is negative to a gravity force. The thermal diffusivity, \( \alpha \), can be evaluated by the following equation:

\[
\alpha = 0.1388 \frac{\rho}{\tau_{1/2}}
\]  

(1)

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Fig. 1 The thermal diffusivity values of three alloys of Zr55Al10Ni5Cu30, Zr60Al15Ni25 and Zr65Al15Cu27.5 in the liquid state.

Fig. 2 Relationship between thermal diffusivity and \((T - T_l)/T_l\) for Zr-based and Pd-based alloys in the liquid state. \(T_l\) is the liquidus temperature.

Fig. 3 Relationship between the estimated thermal diffusivities at liquidus temperature and the critical cooling rate for glass formation \(R_c\) for Zr-based and Pd-based alloys.

3. Results and Discussions

Thermal diffusivity of the Zr55Al10Ni5Cu30 alloy was measured in the liquid state at temperature up to 1218 K with a heating rate of 0.17 K/s. The measurements for Zr60Al15Ni25 and Zr65Al15Cu27.5 alloys were also carried out in the liquid state at temperature up to 1313 K with a heating rate of 0.17 K/s. The results are shown in Fig. 1. The positive temperature dependence was observed in the liquid state for three alloys. These thermal diffusivity values of three alloys in the liquid state can be described as a function of temperature in the following equations.

\[
\alpha_{Zr55Al10Ni5Cu30} = 3.73 \times 10^{-3} (T - 1163) + 4.56 \times 10^{-6} \text{ m}^2/\text{s} \quad 1163 \leq T \leq 1228 \quad (2)
\]

\[
\alpha_{Zr60Al15Ni25} = 3.87 \times 10^{-3} (T - 1223) + 5.03 \times 10^{-6} \text{ m}^2/\text{s} \quad 1223 \leq T \leq 1313 \quad (3)
\]

\[
\alpha_{Zr65Al15Cu27.5} = 4.75 \times 10^{-3} (T - 1193) + 5.41 \times 10^{-6} \text{ m}^2/\text{s} \quad 1193 \leq T \leq 1313 \quad (4)
\]

After Nishi et al.\(^2\) the thermal diffusivity values of three Pd-based alloys are given as follows.

\[
\alpha_{Pd40Cu30Ni10P20} = 5.73 \times 10^{-3} (T - 920) + 3.28 \times 10^{-6} \text{ m}^2/\text{s} \quad 920 \leq T \leq 1120 \quad (5)
\]

\[
\alpha_{Pd40Ni40P20} = 3.95 \times 10^{-3} (T - 1000) + 4.12 \times 10^{-6} \text{ m}^2/\text{s} \quad 1000 \leq T \leq 1120 \quad (6)
\]

\[
\alpha_{Pd40Cu60P20} = 6.67 \times 10^{-3} (T - 1060) + 5.35 \times 10^{-6} \text{ m}^2/\text{s} \quad 1060 \leq T \leq 1120 \quad (7)
\]

In order to compare the results for Zr-based alloy with those of Pd-based alloy, the thermal diffusivity values are summarized as a function of normalized temperature, \((T - T_l)/T_l\), where \(T_l\) is the liquidus temperature in Fig. 2. Moreover, the thermal diffusivity value was determined at liquidus temperature by extrapolating the given equations to that temperature. Then, the results are plotted against the critical cooling rate of each alloy as shown in Fig. 3. The lower the thermal diffusivity values of Zr-based alloys at liquidus temperature, the lower the critical cooling rate to obtain metallic glass phase becomes. This is consistent with the Pd-based alloy case. It is noted that the Pd40Cu30Ni10P20 alloy has the highest glass-forming ability among three Pd-based alloys investigated. It can be concluded that the critical cooling rate to obtain metallic glass phase of this alloy system could be an increasing function of thermal diffusivity.

where \(I\) is the thickness of sample and \(t_{1/2}\) is the time required for the back surface of the sample to reach one half of the maximum temperature rise. The radiative heat loss and the conductive heat loss at the interface between the sample and cell material is negligibly small to obtain reliable value of thermal diffusivity.\(^2,3\)
4. Conclusion

The thermal diffusivity values of three Zr-based alloys of Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$, Zr$_{60}$Al$_{15}$Ni$_{25}$, Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ by the laser flash technique and the results were compared with those of Pd-based alloys. These results suggest that thermal diffusivity of alloy liquids might be an indicator of the glass-forming ability of Zr-based and Pd-based alloys.

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