Thermophysical Properties of Zr-O Liquid Alloys Measured by Electrostatic Levitation

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Abstract

To understand behavior of molten core materials is an urgent issue to investigate the progression of a core meltdown accident in nuclear power plants. Zirconium (Zr) based alloys have been widely used as nuclear fuel claddings and structural materials in the nuclear power plants. Since the typical atmosphere during most accident scenarios is steam, Zr liquid containing significant amount of O (Zr-O liquid alloys) will be generated in the case of the core meltdown accident. In this study we aim to provide thermophysical properties of Zr-O liquid alloys. To avoid a difficulty in measurement due to high melting point and high reactivity of Zr liquid, electrostatic levitation technique was employed for the measurement. Zr-O alloys with nominal compositions of Zr0.2O0.8 and Zr0.8O0.2 were prepared from powder Zr and ZrO2 by solid-state reaction. The oxygen composition was evaluated by thermogravimetric analysis. The measured viscosities of Zr-O liquids are higher than those of Zr liquid (experimental) and ZrO2 liquid (calculated), which indicates that the composition-dependent viscosity may have maxima in Zr-O liquids.

Keywords: Molten core materials, Zr-O liquids, Electrostatic levitation, Viscosity, Surface tension

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1. Introduction

A core melt down accident in a nuclear power plant results in the relocation of the molten core materials 1). The molten core materials solidified to form debris, which has to be removed for the reactor decommission. Therefore, it is important to understand spreading behavior of the molten core materials so that the location of the debris can be predicted. Recent development in the computational simulation allows us to calculate the spreading behavior of liquids based on the physical properties of liquids such as viscosity, surface tension and density 2).

In nuclear reactors, one of the main component is Zirconium (Zr) based alloys, which are widely used as nuclear fuel claddings and structural materials. It is known that Zr has a high affinity to Oxygen (O). Based on the phase diagram 3), solid α-Zr can contain up to 30 at% of O and there is no miscibility gap between Zr and ZrO2 liquids. Since the typical atmosphere during most accident scenarios is steam, Zr liquid containing significant amount of O (Zr-O liquid alloys) will be generated in the case of the core meltdown accident. This means that it is important to understand the physical properties of Zr-O liquid alloys in order to estimate the location of the debris. Therefore, in this study, we aim to provide thermophysical properties of Zr-O liquid alloys.

Since Zr liquid has considerably high chemical reactivity, it is challenging to perform measurement using containers to hold liquid alloys because of the reaction between the liquid alloys and the container. Thus, an electrostatic levitation method 4) was employed in this study for the measurement to avoid the problem regarding the container. In this method, the measurements are performed on the sample levitated by electrostatic force, which allows us non-contact measurements. We have focused on this method and adapted it to Zr-Fe 5), Zr-Cr, and Zr-Ni 6) liquid alloys, which are one of the molten core materials. In this study, we have measured the thermophysical properties of Zr-O liquid alloys using an electrostatic levitation furnace (ELF).

2. Experimental

2.1 Experimental Setup

Since a detailed description of the ELF can be found elsewhere 7-10), only a brief description is given here. A
The surface tension and viscosity were obtained by a drop oscillation method \(^1\). In this method, the decay time and oscillation frequency of the oscillated sample are used for calculating the viscosity and surface tension. The oscillation of the sample was induced by applying the sinusoidal voltage to the top electrode for a short time as shown in Fig. 1(d). The shadow of the oscillated sample was projected on the photo detector with a 4000 Hz sampling frequency equipped with a slit such that the variation in the vertical diameter of the melted sample was measured. The oscillation frequency \(\omega\) and decay time \(\tau\) were obtained from the observed data. The viscosity \(\eta\) and surface tension \(\gamma\) are given by \(^1\)

\[
\eta = \frac{\rho r^2}{5\tau}
\]

\[
\gamma = \frac{\rho r^3 \omega^2}{8}
\]

where \(r\) is the radius of the sample.

In order to know the temperature of the sample, the emissivity of the sample is necessary because the temperature was measured by the single-color pyrometer. Since there is no available information on the emissivity of Zr–O liquid alloys, we determined the emissivity based on the cooling curve. The cooling curve was obtained from the melted sample by turning off the heating laser. We determined the emissivity such that the solidification temperature matched the solidus line in Zr-O phase diagram.

### 2.3 Sample Preparation and Characterization

We selected the compositions of the alloys to be Zr\(_x\)O\(_{1-x}\) (\(x = 0.1\) and 0.2). The raw materials were Zr powder (99.9% purity) and ZrO\(_2\) powder (99.9% purity). The weighed powders were mixed by ball milling and subsequently pressed into pellets under a pressure of 100 MPa. The pellets were heated in vacuum for 24 hours at 1200 °C for the sample with \(x = 0.1\) and at 1400 °C for the sample with \(x = 0.2\), respectively. The sintered pellets were crashed to obtain small pieces with 25–35 mg in weight. These small pieces were arc melted in an Ar atmosphere to obtain spherical samples which were used for ELF experiments.

The Oxygen composition \(x\) of Zr\(_{1-x}\)O\(_x\) was determined by thermogravimetric (TG) analysis. The Zr\(_{1-x}\)O\(_x\) sample was oxidized to ZrO\(_2\) by heating the sample in air, and the initial oxygen composition \(x\) was estimated from the mass increase. The measurements were performed before and after ELF experiment. Before the ELF experiments, three spherical samples were arbitrarily selected, and their oxygen compositions were measured via TG. From the measured data, the averaged value and the standard deviation were calculated.

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**Fig. 1** Hardware arrangement the (a) ELF, (b) sample position control, (c) sample imaging system and (d) drop oscillation induction and observation system: (1) sample, (2) top electrode, (3) bottom electrode, (4) side electrodes, (5) He–Ne lasers, (6) position detectors, (7) CO\(_2\) lasers, (8) pyrometers, (9) photo detector, (10) charge-coupled device (CCD) camera with a telephoto objective lens, and (11) ultraviolet background light.
After the ELF experiments, the samples used for the ELF experiments were analyzed via TG in the same way.

3. Results and Discussion

Figures 2 show the oxygen composition \(x\) of \(\text{Zr}_{1-x}\text{O}_x\) measured before and after ELF experiments. The oxygen compositions before ELF experiments were 0.18 ± 0.03 and 0.24 ± 0.02 for \(\text{Zr}_{1-x}\text{O}_x\) \((x = 0.1\) and 0.2\), respectively, which were higher than those of the initial compositions, possibly because of the surface oxidation of the raw Zr powder. Since the raw Zr powder was stored in water, the Zr particles were covered by thin oxide layers. The oxygen composition after ESL experiments were roughly agree with those before ELF experiments. Thus, we assumed that there was no significant variation in the oxygen composition during ELF experiments. To avoid confusion, the notations of the samples are not changed although the initial composition and the composition before ELF experiment do not match.

Figure 3 shows the temperature-dependent density of liquid \(\text{Zr}_{1-x}\text{O}_x\) together with the literature values of liquid Zr\(^8\) and ZrO\(_2\)\(^{12}\). Two samples were measured for each composition, and the data are in good agreement indicating the high reproducibility of the measurement. The density linearly decreases with increasing temperature. This linear temperature dependence is generally observed in liquid metals and alloys. The density values of liquid \(\text{Zr}_{1-x}\text{O}_x\) lie between the densities of liquid Zr and ZrO\(_2\).

The molar volumes of Zr-O liquid alloys at 2100 °C are given in Fig. 4 as a function of the oxygen composition \(x\). The density of ZrO\(_2\) at 2100 °C was estimated by linear extrapolation of the data reported by Kohara et al\(^{12}\). The oxygen compositions determined by TG analysis are used to plot the data for \(\text{Zr}_{1-x}\text{O}_x\) \((x = 0.1\) and 0.2\). The molar volume of Zr-O liquid alloys linearly varies with the oxygen composition, indicating that the volume becomes a simple linear combination of Zr and ZrO\(_2\), which is usually referred to as Vegard’s law in solid solution\(^{13}\).

![Fig. 2] Oxygen composition \(x\) determined by a thermogravimetric method before and after ELF experiments for (a) \(x = 0.1\) and (b) \(x = 0.2\), respectively. The standard deviations are shown as error bars.

![Fig. 3] Temperature dependent density of liquid \(\text{Zr}_{1-x}\text{O}_x\). Two samples were measured for each composition. The solid lines represent the experimentally obtained literature values of liquid Zr\(^8\) and ZrO\(_2\)\(^{12}\). The dashed line is the linear extrapolation.

![Fig. 4] Molar volume of liquid \(\text{Zr}_{1-x}\text{O}_x\) at 2100 °C as a function of the oxygen composition \(x\). The dashed line is for eye guide.
Figure 5 shows the temperature dependent viscosity of liquid Zr<sub>1-x</sub>O<sub>x</sub> (<i>x</i> = 0.1 and 0.2), together with the literature values of liquid Zr<sup>10</sup> and ZrO<sub>2</sub> <sup>121</sup>. Since the total number of the measurement points exceeds 100, only the averaged values and standard deviations are shown in the figure. The viscosity of Zr was obtained experimentally using the same ELF while that of ZrO<sub>2</sub> is an estimated value based on a molecular dynamic calculation. Although the scattering of the measured values is large, it can be said that the viscosities of Zr<sub>1-x</sub>O<sub>x</sub> (<i>x</i> = 0.1 and 0.2) are large than that of Zr. Assuming that the estimated viscosity of ZrO<sub>2</sub> is correct, the viscosities of Zr<sub>1-x</sub>O<sub>x</sub> (<i>x</i> = 0.1 and 0.2) are large than both Zr and ZrO<sub>2</sub>, suggesting that there is a maximum in the oxygen composition dependent viscosity of Zr-O liquid alloys.

The viscosity of binary liquid alloys η<sub>i</sub> can be expressed using the excess viscosity η<sub>e</sub> by

\[
η_i = (x_1η_1 + x_2η_2) + η_e
\]  

(3)

where \(x_i\) is the mole fraction and \(η_i\) is the viscosity of component \(i\). The oxygen composition dependent viscosity of Zr-O liquid alloys indicates that \(η_e\) is positive for Zr-O. Based on a phenomenological equation proposed by Iida et al., \(η_e\) is a function of the diameter and the mass of the constituent atoms, and the activity coefficient of component \(x_i\). The \(η_e\) tends to become positive as the difference of atomic mass and atomic radius increases of the constituent atoms, and the excess Gibbs energy of mixing \(G_e\) becomes more negative. Zr-O alloys have negative \(G_e\) due to the high affinity of Zr to O, which might explain the positive \(η_e\) for Zr-O.

The measured surface tensions of liquid Zr<sub>1-x</sub>O<sub>x</sub> (<i>x</i> = 0.1 and 0.2) are shown in Fig. 6, together with the literature value of liquid Zr <sup>8</sup>. The surface tension of liquid ZrO<sub>2</sub> has not been reported. While the measured values of the surface tension of the two samples, Zr<sub>0.9</sub>O<sub>0.1</sub> #3 and #4 agree well each other, those of Zr<sub>0.8</sub>O<sub>0.2</sub> rather scatter, especially at 2160 °C. Since the surface tension is governed by the surface conditions of materials, slight amount of the oxygen detachment during the ELF experiments might affect the measurement results. Oxygen atoms tend to attach to the surface of materials at lower temperature, which may explain the larger scatter at lower temperature. The values for the surface tension of Zr<sub>1-x</sub>O<sub>x</sub> (<i>x</i> = 0.1 and 0.2) liquid alloys are lower than that of Zr.

4. Conclusion

In the present work, the thermophysical properties of Zr<sub>1-x</sub>O<sub>x</sub> (<i>x</i> = 0.1 and 0.2) liquid alloys have been measured using an electrostatic levitation technique. The results obtained indicate that the molar volume becomes a simple linear combination of Zr and ZrO<sub>2</sub>. The viscosity increases and the surface tension decreases compared to those of pure Zr.

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**References**

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