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ジルカロイ融体の表面張力に及ぼす温度と酸素の影響

Effects of Temperature and Oxygen on Surface Tension of Molten Zircalloy

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1. Introduction

In preparation of unexpected accident in nuclear power plant, numerical calculations have been conducted to elucidate the behavior of core-melting and relocation. An accurate surface tension data of molten zircalloy (Zry) used as the fuel cladding tube is required to obtain reliable calculation results. In order to measure surface tension of molten metallic melt, it is crucial to suppress contamination of sample such as chemical reaction with the supporting materials and oxygen adsorption from the measurement atmosphere. Oxygen is well known as strong surfactant for metallic melt [1-5]. Since zirconium that is a main component of Zry has a very high oxygen solubility [6-12], surface tension of molten Zry may show the time dependence due to increase in oxygen content in the sample as in the case of molten titanium [13].

In the present study, surface tension of molten zirconium and Zr–1.7 mass%Sn alloys that is a dummy of Zry was measured free of contamination from container even at high temperature sufficiently above the melting point in consideration of influence of oxygen partial pressure, P_{O_2}, of atmospheric gas.

2. Experimental method

A cube of zirconium and Zr–Sn alloy was electromagnetically levitated and then melted under a mixture of high-purity Ar–He gas with P_{O_2} 10^{-2} Pa flowing at 2 L·min^{-1}. A mixture gas of H_2–CO_2 was also used as the flowing atmospheric gas to control the P_{O_2} at 10^{-4} and 10^{-6} Pa through their gas phase equilibrium. The P_{O_2} of the gas was confirmed by a zirconia oxygen sensor operated at 1008 K at the inlet of chamber. The sensors were calibrated using the gas phase equilibrium of H_2–CO_2 and in-situ observation of oxidation/reduction reactions of several metals [14]. Semiconductor laser heating was superimposed on the levitated droplet to heat it very high temperature. The temperature and the oscillation behavior of the levitated droplets were monitored from above, using a high-speed video (HSV) camera and a monocolor pyrometer.

The frequencies of the surface oscillation of $m = 0, \pm 1$, and ± 2 for the $l = 2$ mode and motion of the center of gravity were analyzed through fast Fourier transformation (FFT) from the HSV images, in consideration of droplet rotations. The surface tension of the droplet was calculated from these frequencies by the Rayleigh equation [15] and Cummings and Blackburn calibration [16]. Since uncertainty contribution of density is small in the calculation of surface tension using the oscillating droplet method using the EML, the following temperature dependence of density of zirconium[14] was used for the calculation in this study.

$$\rho = 6240 - 0.29(T - 2128) \qquad (1)$$

3. Results and discussion

Figure 1 shows the time dependence of sample mass and corresponding the surface tension of molten zirconium and Zr-1.7mass%Sn alloy when it was maintained at 2300 K under flowing Ar–He–O_2 gas and Ar–He–H_2–CO_2 gas using EML. When the molten zirconium and Zr-Sn alloy were maintained under a flowing mixture of Ar–He–H_2–CO_2 gas at P_{O_2} of 10^{-6} Pa (■, ▲), the sample mass increases with time, resulting in a decrease in surface tension. This implies that atmospheric oxygen gas dissolves into the molten sample during heating the sample. When the P_{O_2} is increased to 10^{-4} Pa, increase in the sample mass and corresponding the decrease in surface tension are promoted. Even though P_{O_2} is further increased to 10^{-2} Pa using Ar–He–O_2 gas, the sample mass and corresponding the surface tension show almost constant even after 20 minutes (□, △). This suggests that the flow rate of the Ar–He–O_2 gas is the rate-determining step for oxygen dissolution in liquid zirconium, while the gas phase equilibrium between H_2 and CO_2 gases continuously supplies oxygen into the molten sample under Ar–He–H_2–CO_2 gas.

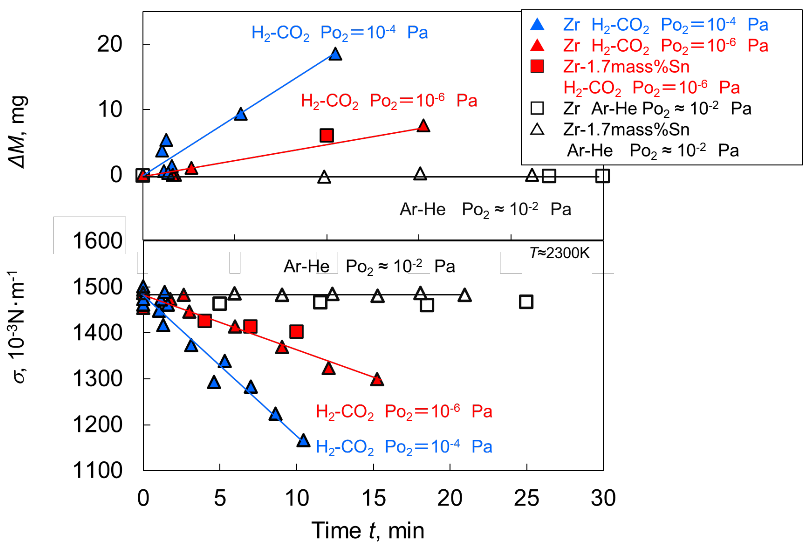

Figure 1. Variations of sample mass and corresponding the surface tension of molten zirconium (△, ▲, ▲) and Zr-1.7mass%Sn (□, ■, ■) with time when the sample was maintained at 2300 K under atmospheric gases of Ar-He and Ar-He-H_2-CO_2.

4. Summary

The surface tension of molten zirconium and Zr-1.7 mass%Sn alloy that is the dummy of Zry was measured by oscillating droplet method using EML. The sample mass was increased with time and corresponding the surfaced tension was decreased when P_{O_2} was 10^{-4} and 10^{-6} Pa under Ar–He–H_2–CO_2 gas. Although P_{O_2} was increased to 10^{-2} Pa using Ar–He–O_2 gas, no detectable variation in the sample mass and the surface tension were confirmed since the flow rate of the gas became the rate-determining step for oxygen dissolution in molten sample.

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