FP Chemistry in a High Temperature Region of LWR under a Severe Accident
(6) Improvement of Ruthenium Release Model from a Nuclear Fuel under a LWR Severe Accident

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Abstract: To improve the ruthenium (Ru) release model from a nuclear fuel in a severe accident, we investigated the vaporization behaviors of Ru from Mo-Ru-Pd-Rh alloys, and derived the activity coefficient of Ru ($\gamma_{Ru}$) in Ru0.725Pd0.160Rh0.115 alloy.

Keywords: Ruthenium, Mo-Ru-Pd-Rh, Vaporization, Activity coefficient

1. Introduction
The precise simulation of Ru release from a nuclear fuel in a severe accident is of vital importance due to its potentially high radiological impact. The Ru usually exists as Mo-Ru-Pd-Rh-Tc alloys precipitates in the nuclear fuel, and its release rate-limiting processes are believed to be the transfer of alloys into open fuel porosities and then Ru vaporization into the bulk atmosphere.[1] Several simulation models of the Ru vaporization from alloys in open fuel porosities have been established. However, the effect of alloy on vaporization is not considered in the models, for example approximately assuming the vaporization coefficient of bulk atmosphere. [1] Therefore, to improve the Ru release model, the $\gamma_{Ru}$ in alloys was determined by analyzing the vaporizing rates of Ru from Ru and Mo-Ru-Pd-Rh alloy powders experimentally obtained in this study.

2. Experimental method
The alloy with the composition of Mo0.231-Ru0.558-Pd0.123-Rh0.088 in molar fraction was prepared by powder metallurgy method as a typical composition of alloys formed in irradiated LWR fuel. The Ru and alloy powder specimens were subjected to TG-DTA, and then Ar-5%H2 was introduced to avoid oxidation of the specimen during the temperature rising process. After reaching the equilibrium condition with no change in weight at a constant temperature, from 1473 to 1773 K to simulate the initial temperatures of fuel in accidents, the atmosphere was switched to air or Ar-1% O2.

3. Results and discussion
For Ru powders, a linear relationship was found between the vaporizing rate of solid Ru (or RuO2) when the Ru can be oxidized to RuO2 on molar basis and overall equilibrium vapor pressures of various gaseous ruthenium oxides ($P_{RuOx}$) over Ru (or RuO2), as shown in Figure 1. For alloy powders, the Mo in alloy was confirmed to be quickly oxidized and vaporized, followed by the oxidation and vaporization of Ru in Mo-free alloys of Ru0.725Pd0.160Rh0.115 as shown in Figure 2. About the vaporization of Ru in alloy when solid RuO2 cannot be formed, the vaporization loss rate ($10^{-5}$mol/h) in alloys can be determined by the following equations.

$\Delta G^o_{(1)} = R \ln \left( \frac{P_{RuO2}}{P_{O2}^{1/2} \gamma_{Ru} X_{Ru}} \right)$

where the $\Delta G^o_{(1)}$, $R$, $T$, $P_{O2}$, $\gamma_{Ru}$ and $X_{Ru}$ refer to molar standard Gibbs energy, gas constant, temperature, oxygen partial pressure, and activity and molar fraction of Ru, respectively. Assuming the vaporization coefficient of Ru equals that of alloys, based on the obtained linear relationship between vaporizing rate of Ru and $P_{RuOx}$, and Equation (2), at one known temperature and atmosphere, Equation (4) can be obtained.

$\nu_{Ru}^{alloy} / P_{RuOx}^{alloy} / P_{RuO2}^{alloy} = 1 / \gamma_{Ru}$

where $\nu_{Ru}^{alloy}$, $P_{RuOx}^{alloy}$ and $P_{RuO2}^{alloy}$ are vaporizing rate of Ru from Ru and alloy powders, $P_{RuOx}$ over Ru and alloy powders, respectively. By Equations (3) and (4), the arithmetic average of $\gamma_{Ru}$ in Ru0.725Pd0.160Rh0.115 alloy was derived to be 1.19 in the temperature range from 1483 to 1673 K.

4. Conclusions
The arithmetic average of $\gamma_{Ru}$ in Ru0.725Pd0.160Rh0.115 alloy was first estimated to be 1.19 in the temperature range from 1483 to 1673 K, which can be used to improve the simulation precision of Ru release models.

Reference