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 (γ_{Ru}) in $Ru_{0.725}Pd_{0.160}Rh_{0.115}$ 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 taking activity coefficient of Ru (γ_{Ru}) in alloys as unity.[1] Therefore, to improve the Ru release model, the γ_{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 $Mo_{0.231}$-$Ru_{0.558}$-$Pd_{0.123}$-$Rh_{0.088}$ in mole 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%H_2 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 changed to air or Ar-1% O_2.

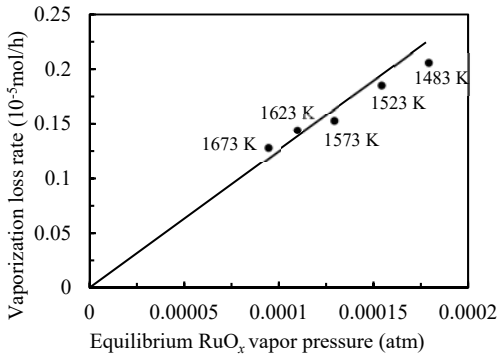

Fig. 1. Relationship between vaporizing rate and equilibrium RuO_x vapor pressure in Ar-1% O_2.

3. Results and discussion

For Ru powders, a linear relationship was found between the vaporizing rate of solid Ru (or RuO_2 when the Ru can be oxidized to RuO_2) on molar basis and overall equilibrium vapor pressures of various gaseous ruthenium oxides (P_{RuOx}) over Ru (or RuO_2), as shown in Figure 1. For alloy powders, the Mo in alloy was confirmed to be quickly and completely vaporized, followed by the oxidation and vaporization of Ru in Mo-free alloys of $Ru_{0.725}Pd_{0.160}Rh_{0.115}$ as shown in Figure 2. About the vaporization of Ru in alloy when solid RuO_2 cannot be formed, the P_{RuOx} over the alloy can be determined by the following equations.

$$Ru(s) + (x/2)\,O_2(g) = RuO_x(g)\ (x=0, 1, 2, 3 \text{ or } 4) \quad (1)$$

$$\Delta G^{o}_{(1)} = -RT\ln\left(P_{RuO_x} \Big/ P_{O_2}^{x/2} \cdot a_{Ru}\right) \quad (2)$$

$$a_{Ru} = \gamma_{Ru} \cdot X_{Ru} \quad (3)$$

where the $\Delta G^{o}_{(1)}$, R, T, P_{O2}, a_{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.

$$v^{Ru}_{Ru} / v^{alloy}_{Ru} = P^{Ru}_{RuO_x} / P^{alloy}_{RuO_x} = 1/a_{Ru} \quad (4)$$

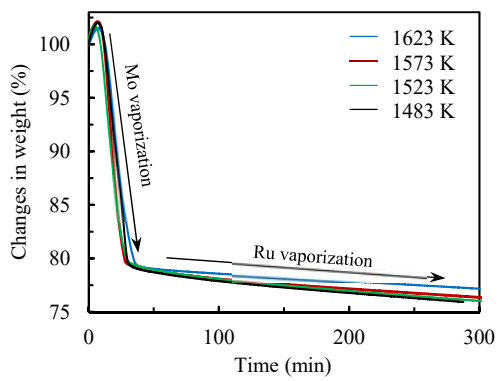

Fig. 2. Weight changes of Mo-Ru-Pd-Rh alloy powders in Ar-1% O_2.

where v^{Ru}_{Ru}, v^{alloy}_{Ru}, $P^{Ru}_{RuO_x}$ and $P^{alloy}_{RuO_x}$ 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 γ_{Ru} in $Ru_{0.725}Pd_{0.160}Rh_{0.115}$ alloy was derived to be 1.19 in the temperature range from 1483 to 1673 K.

4. Conclusions

The arithmetic average of γ_{Ru} in $Ru_{0.725}Pd_{0.160}Rh_{0.115}$ 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

[1] G. Brillant, C. Marchetto, and W. Plumecocq, Ann. Nucl. Energy, 61 (2013) 88-95.