Measurement of ruthenium activity in ruthenium-palladium-rhodium alloys

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Abstract: For improvement of the existing ruthenium (Ru) release model from fuel under a severe accident, Ru activity (a_{Ru}) of Ru-palladium (Pd)-rhodium (Rh) alloys was experimentally determined by a new method using thermogravimetric analysis (TGA).
Keywords: Ru-Pd-Rh, Thermogravimetric analysis, Oxidative vaporization, Ruthenium activity

1. Introduction

Due to the potentially high radiological impact of Ru under a severe accident, several simulation models for its release from a nuclear fuel have been proposed during the past decade [1]. However, all these models neglect the effect of molybdenum (Mo)-Ru-Pd-Rh-technetium (Tc) alloys on Ru release, namely taking the a_{Ru} in alloys as unity. On the other hand, the a_{Ru} of Ru-containing alloys cannot be evaluated by the traditional methods, such as Knudsen cell mass spectrometry, due to the difficulty to measure vapor pressures of gaseous Ru oxides (RuO_x). Therefore, the objective of present study is to develop a new method for determining a_{Ru} in Mo-Ru-Pd-Rh alloys using TGA. Since the oxidative vaporization of Ru mainly occurs after the total oxidation of Mo in alloys [2], a_{Ru} in Ru-Pd-Rh was investigated in the present study. The evaluation result of a_{Ru} was validated by comparing the thermodynamic calculation result.

2. Experimental procedure

The Ru-Pd-Rh alloy powders with the mole fraction ratio of 0.726/0.160/0.114 were prepared by powder a metallurgy method as a typical elemental ratio of Ru, Pd and Rh in alloys formed in an irradiated LWR fuel [3]. The Ru and alloy powder specimens were subjected to the TGA. During the temperature rising process, Ar-5% H_2 was introduced to avoid the oxidation of specimens. After reaching the equilibrium condition with no change in weight at predetermined temperatures, the atmosphere was changed to Ar-1.0% O_2 or Ar-3.0% O_2 or Ar-4.5% O_2. The predetermined temperatures were from 1483 to 1673 K to simulate the initial temperatures of fuel under accidents.

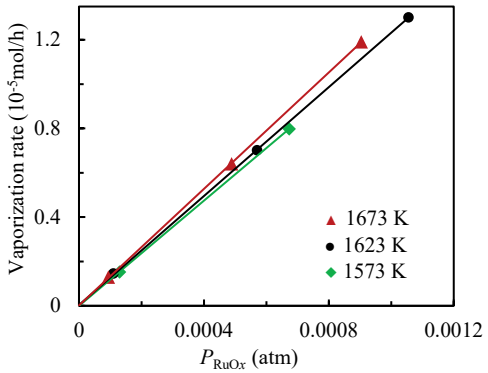

Fig. 1. Relationship between vaporizing rate of Ru powders and P_{RuOx} at different temperatures.

3. Determination of the Ru activities in the alloys

It is well known that under the same temperature and oxygen partial pressure, the a_{Ru} of alloys is proportional to the equilibrium vapor pressures of various RuO_x gases (P_{RuOx}). Figure 1 shows the correlation between the vaporizing rate of solid Ru and P_{RuOx} [4] over powders. This result shows that there is a linear relationship between them. On the other hand, the phase diagram of Ru-Pd-Rh system [5] shows that the composition of alloy powders during TGA changed along the tie line emanated from vertex of Ru in the (α + ε) coexistence phase in this temperature condition. This indicates the a_{Ru} of alloy powders should be constant during vaporization of Ru in this phase. Therefore, as a new method, the a_{Ru} of alloys were calculated by using the ratio of vaporization rate of alloy powders to that of Ru powders under same experimental condition.

Figure 2 compares the calculated a_{Ru} for the Ru-Pd-Rh system (Pd/Rh = 1.4, molar ratio) in (α + ε) phase with thermodynamic calculation results [5]. The measured a_{Ru} slightly increases with an increase in temperature and is just a little smaller than the values obtained by thermodynamic calculation. This result indicates that the new methods for Ru activity in this condition is valid.

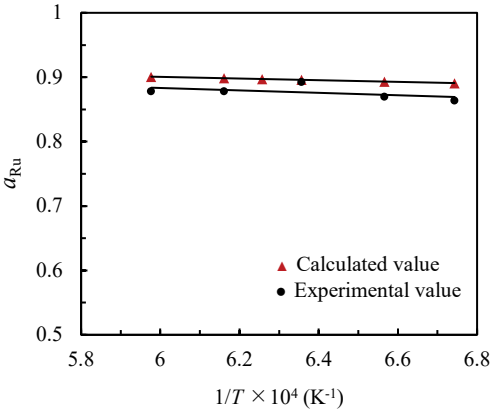

Fig. 2. Dependence of a_{Ru} on temperature for the Ru-Pd-Rh system (Pd/Rh = 1.4, molar ratio) in (α + ε) phase.

4. Conclusions

A simple method has been developed to experimentally determine the a_{Ru} in the Ru-Pd-Rh system, which has been confirmed to slightly increase with increasing temperature from 1483 to 1673 K as expected by the thermodynamic calculation.

Reference

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