Fundamental Research on Fission Product Chemistry
(2) Evaluation of Oxidation and Vaporization Behavior of Ruthenium and Molybdenum Alloys in a Nuclear Fuel

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Abstract: For a more accurate evaluation of Ru and Mo release behavior from fuel under severe accident conditions, Ru and Mo oxidation and vaporization behaviors were investigated by thermogravimetric-differential thermal analysis (TG-DTA). The results gave fundamental data of the Ru and Mo release behavior.
Keywords: Ruthenium, Molybdenum, Oxidation, Vaporization

1. Introduction

The so-called "white inclusions" composed of molybdenum (Mo), ruthenium (Ru), palladium (Pd), rhodium (Rh) and technetium (Tc) system are formed in irradiated UO_2 and (U, Pu)O_2 fuels[1]. Among the elements in this system, Ru and Mo behaviors under severe accident conditions such as release behavior from fuel are important especially because of potentially high radiotoxicity under air and affinity with cesium, respectively. Although some data on the release behavior of Ru and Mo with atmosphere-dependence were reported, release mechanism is still unclear and the release model considering the formation of alloys has not been established. Therefore, for an accurate evaluation of release behavior of Ru and Mo from fuel under severe accident conditions, we started the research on the Ru and Mo release behavior from Mo-Ru-Rh-Pd alloys system. As the first step, we investigated the oxidation and vaporization behavior of the Mo and Ru in the oxidizing atmosphere.

2. Experimental method

The metallic powder specimens of Mo and Ru were subjected to the TG-DTA to evaluate the oxidation and vaporization properties. During the temperature rising process, Ar-5%H_2 atmosphere was adopted to avoid oxidation of the specimen. After reaching the equilibrium condition with no change in weight at a constant temperature, from 1473 to 1773 K, the atmosphere was changed to air. The samples after TG-DTA were characterized by XRD and SEM-EDS.

3. Results and discussion

Figure 1 shows the relative changes in weight for the Mo and Ru powders in air during the TG-DTA. The changes in weight gain and loss are associated with mainly oxidation and vaporization, respectively.

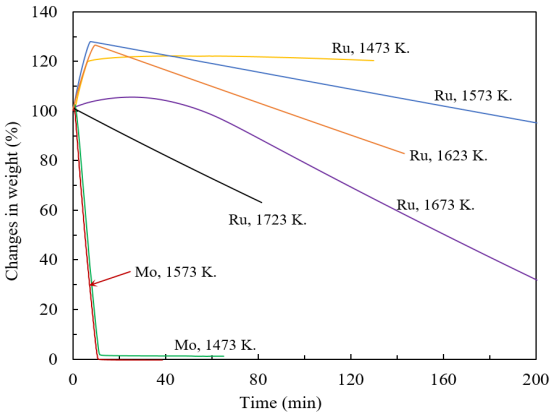

Fig. 1. Weight change of Mo and Ru powders in air.

The steep changes in weight loss for Mo powders are observed at 1473 and 1573 K. The weight loss rates are nearly the same due possibly to the instantaneous formation of high volatile $(MoO_3)_x$ (g) by oxidation of Mo.

Above 1573 K, the weight gain rates for Ru decreased with increase of temperature due to the enhancement of vaporization concurrent with oxidation. By a thermodynamic consideration, the predominant reaction products for oxidation of Ru are RuO_2(s) and RuO_3(g) below 1700 K and only RuO_3(g) above 1700 K in air, which corresponds to the results at 1723 K that weight gain was not observed. It should be noted that above 1573 K, the weight loss rates of each Ru samples became constant as shown in Figure 1, although the total surface area of powders changed with the vaporization of samples. Figure 2 shows the correlation between vaporization rates and equilibrium RuO_3 vapor pressure [2] above RuO_2 below 1700 K and Ru above 1700 K. The weight loss rates are approximately proportional to the equilibrium RuO_3 vapor pressure, which suggests that the formation reaction of RuO_3 is very fast and the gases around the sample achieve in equilibrium immediately with the sample.

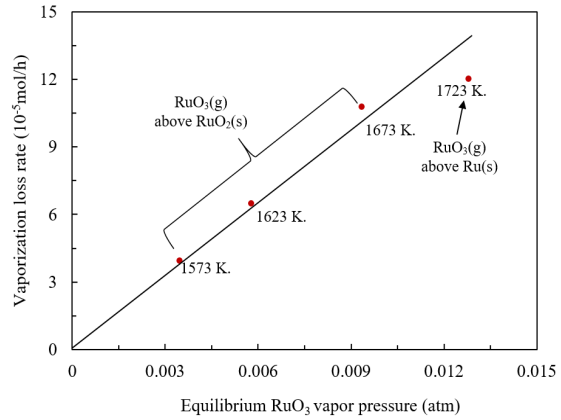

Fig. 2. Relationship between vaporizing rate and equilibrium RuO_3 vapor pressure.

4. Conclusions

The oxidation and vaporization rates of Mo powders are much bigger than that of Ru powders. The vaporization rates of Ru powders are controlled by the equilibrium RuO_3 vapor pressure.

References

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