Oxidation and evaporation behaviors of Mo under severe accident conditions

*Jiazhan Liu[1], Kunihisa Nakajima[1], Shuhei Miwa[1], Hidetoshi Karasawa[1] and Masahiko Osaka[1]
[1]Japan Atomic Energy Agency (JAEA)

Abstract: To construct a precise Mo release model in severe accident (SA), oxidation and evaporation behaviors of Mo powders were investigated by the thermogravimetric analysis (TGA) technique. The experimental results showed that oxidation and evaporation rates of Mo were influenced by oxygen diffusion rates in gas phase and solid MoO_2 layer formed on the surface of Mo powders. Mechanism of these diffusions were discussed.
Keywords: Mo, Oxidation, Evaporation, Oxygen diffusion

1. Introduction

The accurate evaluation of release behaviors of fission products (FPs) from nuclear fuel in SA is crucial for the improvement of source term. As one of the FP elements, Mo has a high fission yield (~ 25%) and can be largely released from fuel under oxidizing conditions by forming MoO_3 polymers gases ($(MoO_3)_x$). Moreover, owing to its high reactivity, Mo can influence the release of some other FPs (such as Cs, Sr and Ba) by forming compounds with them. Our previous research confirmed that solid Mo/MoO_2 couple could retard the release of Ru by controlling the oxygen potential of Mo-Ru-Pd-Rh-Tc alloy precipitates in fuel [1]. Consequently, it can be concluded that for source term it is essential to construct a model to comprehensively simulate the release process of Mo from fuel. For this purpose, oxidation and evaporation behaviors of Mo powders under severe accident conditions were investigated by the TGA technique in this study.

2. Experimental method

For one experiment, about 0.03 g of Mo powder sample was loaded into an alumina crucible and then inserted to the thermogravimetry. During the temperature rising process, Ar-5% H_2 was introduced horizontally over the opened top of crucible to avoid oxidation of the sample. After reaching the equilibrium condition with no change in weight at a constant temperature from 1473 to 1673 K, the atmosphere was changed to Ar-1% O_2 or Ar-0.1% O_2. The sample weight was continuously monitored. After several hours, the atmosphere was changed back to Ar-5% H_2 to reduce the condensed Mo oxides to the metallic state. This operation was conducted to obtain the weight of these condensed Mo oxides by mass balance calculation.

3. Results and discussion

Fig. 1 shows the wight changes of Mo samples during TGA. Our previous study confirmed that MoO_2(s) was formed during TGA [1]. Hence, the initial weight change of sample can be attributed to the oxidation of Mo to MoO_2(s) and then to $(MoO_3)_x$ (g) . The weight loss after changing atmosphere to Ar-5% H_2 should result from the reduction of MoO_2(s) to Mo.

For the evaporation process of the formed MoO_2(s), it can be divided into three steps: (1) transfer of O_2(g) to powder surfaces, (2) evaporation reactions and (3) transfer of vapors away from powder surfaces. Under experimental atmospheres, the overall equilibrium vapor pressures of various $(MoO_3)_x$ were higher than 1 atm [2], which correspond to a evaporation rate of sample larger than 100 mg/min in thermogravimetry. However, the actual evaporation rate of sample shown in Fig. 1 is very slow, indicating the $(MoO_3)_x$ vapors over powders were not in equilibrium with powders. Therefore, we inferred that transfer of O_2(g) to powder surfaces is the rate-controlling step. To validate this assumption, the following equation was used to calculate the actual partial pressure of O_2(g) over powders ($p^s_{O_2}$).

$$v_{O_2} = \frac{D_{O_2,Ar}(p_{O_2} - p^s_{O_2})S}{RTh} \quad (1)$$

where v_{O_2} is the average diffusion rate of O_2(g) and can be obtained by mass balance calculation using weight changes of sample (Fig. 1), $D_{O_2,Ar}$ the diffusion coefficient of O_2(g), p_{O_2} the oxygen partial pressure on top of crucible, S the cross section area of crucible, T the temperature and h the diffusion length of O_2(g). The calculated values of $p^s_{O_2}$ under experimental atmospheres of Ar-1% O_2 and Ar-0.1% O_2 were about 10^{-3} atm and smaller than 10^{-5} atm, respectively. It can be thought that there was a large oxygen concentration gradient on the diffusion path of O_2(g). Therefore, the rate-controlling step for evaporation of MoO_2(s) is the transfer of O_2(g) to powder surfaces.

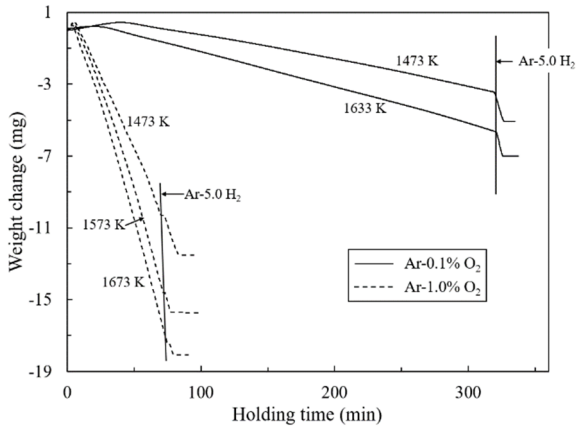

Fig. 1. Weight change of samples during TGA.

The small weight loss amount after changing atmosphere to Ar-5% H_2 indicates a majority of Mo still left inside powders. For the oxygen partial pressure in powders, it should be controlled by the Mo/MoO_2 couple and therefore smaller than $p^s_{O_2}$. Hence, there is another oxygen concentration gradient in the MoO_2 layer formed on the surface of Mo. Consequently, the oxidation and evaporation rates of Mo were thought to be influenced by oxygen diffusion rates in the gas phase and the formed MoO_2 layer.

Reference

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