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Letter to the Editors

Oxidation behavior of U–10 wt% Mo alloy in air at 473–773 K

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Abstract

The oxidation behavior of U–10 wt% Mo alloy was studied using an XRD and a thermogravimetric analyzer in the temperature range from 473 to 773 K in air. It was found from the XRD study that U–10 wt% Mo alloy was completely converted to U_3O_8 at temperatures above 673 K. The oxidation rate of U–10 wt% Mo was lower than that of uranium. The activation energy for oxidation of U–10 wt% Mo was determined to be 66.64 kJ/mol in the temperature range of 473–773 K and it was higher than that of uranium.

1. Introduction

The conversion from high enriched uranium (HEU) to low enriched uranium (LEU) for use in research reactor fuel requires higher fissile uranium per unit volume to compensate for the reduction in enrichment. There have been some efforts to develop a new fuel material by replacing HEU with LEU with stable irradiation behavior, a very dense fuel dispersant (>15 g-U/cm^3) and a very high volume loading in the dispersant (>50 vol.%). U–Mo alloy has been considered to be a prime candidate for dispersion fuel for research reactors to meet these conditions. Knowledge of the oxidation behavior of U–Mo alloy in various atmospheres is necessary to evaluate their stability.

There have been many studies of the oxidation of uranium metals [1–8] and some uranium alloys [9–16]. Loriers [1] carried out research on the oxidation of metallic uranium at ordinary temperatures and at burning temperatures. Leibowitz et al. [2,3] studied oxidation rates in the temperature range from 398 to 523 K in oxygen pressures between 20 and 800 mm Hg. Bennett et al. [5–7] carried out an experiment to investigate the influence of aluminum content, water vapor and swelling on oxidation behavior of irradiated and unirradiated uranium. Ritchie [8] reviewed the reactions of uranium with oxygen and water vapor under various conditions. Antill and Peakall [9] reported for the oxidation of uranium alloys in carbon dioxide and in air that additions of titanium, molybdenum, niobium and copper reduced the attack in air at 773 K by factors up to 200, whereas the silicon alloys had a high rate of attack in carbon dioxide at most temperatures. Greenholt and Weirick [10] carried out the oxidation of uranium–0.75 wt% titanium in atmosphere containing oxygen and/or water vapor at 413 K. Kang et al. [11] studied the oxidation behavior of U_3Si in air at 523–673 K. Barnartt et al. [12] carried out the oxidation of 50 wt% uranium–zirconium alloy with oxygen gas at 1 atm pressure over the range of 473–773 K. Matsui et al. [13,14] investigated the oxidations of U–10 at.% Zr and U–20 at.% Zr in air at 432–1028 K and 422–1063 K, respectively. Rama Rao et al. [15] observed the oxidation behavior of U–Zr alloys having different concentrations from 10 to 90 at.% Zr in atmospheric condition. However, there are no data on the oxidation behavior of U–Mo alloy in the temperature range of 473–773 K.

In the present paper, the oxidation behavior of U–10 wt% Mo alloy was studied by XRD and thermogravimetry in the temperature range of 473–773 K in air.

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2. Experiment

The U–Mo alloy used in this study was prepared with 99.9% pure depleted uranium and 99.7% pure molybdenum. Powder of this alloy was produced using a KAERI-designed centrifugal atomizer [16]. Complete descriptions of the fabrication method and characterization results have been provided early by Kim et al. [17]. The average density and specific surface area of U–10 wt% Mo used in this study are 16.8 g/cm^3 and 5×10^{-2} cm^2/mg, respectively.

The oxidation test was performed using a thermogravimetric analyzer (TG-171, Cahn) under isothermal conditions. The U–10 wt% Mo alloy powder was contained in a platinum crucible and heated up to the test temperature in a flow of purified helium. While the oxidation test was performed, the oxidant, air, was continuously injected. The weight gain of the sample was measured by a microbalance having a load-carrying capacity of 100 g of samples and sensitivity of 1 μg, and the data were automatically acquired and stored along with time and temperature during the oxidation. The flow rate of oxidizing gas was 40 cc/min at atmospheric pressure.

3. Results and discussion

It is generally known that there are stable uranium oxides of UO_2, U_4O_9, U_3O_8 and UO_3 and metastable uranium oxides of U_3O_7 and U_2O_5. After the oxidation tests the oxide forms of U–10 wt% Mo alloy were confirmed with XRD patterns. UO_2 and U_3O_7 were detected after 40 h at a temperature 473 K and U_3O_8 began to be detected at 573 K. UO_2 and U_3O_7 were not detected at temperatures above 673 K and only U_3O_8 was detected. This result is in agreement with result from Ritchie [8]. He reviewed that at temperatures up to 473 K, the oxide formed was hyperstoichiometric uranium dioxide (UO_{2+x}) with x in the range of 0.2–0.4, while U_3O_8 was formed at higher temperature (>548 K). Fig. 1 shows oxidation data obtained in this study over the temperature range of 473–773 K. The oxidation rates of uranium and its alloys have been analyzed by various equations such as linear, parabolic and paralinear depending on oxidation conditions. The fraction reacted (α) is shown as a function of time in Fig. 1.

Weight gain per unit area by oxidation of uranium can be expressed using the following a kinetic law:

$$(\Delta w/A) = kt^n, \tag{1}$$

where $(\Delta w/A)$, t, k and n represent weight gain in mg/cm^2, time in hours, reaction rate constant in mg/h cm^2 and constant, respectively. If n is 0.5 the oxidation mechanism is controlled by diffusion through the reaction layer and if n is 1 it is controlled by surface reaction. The weight gain per unit area, $\Delta w/A$, during oxidation is plotted against time in log–log scale in Fig. 2.

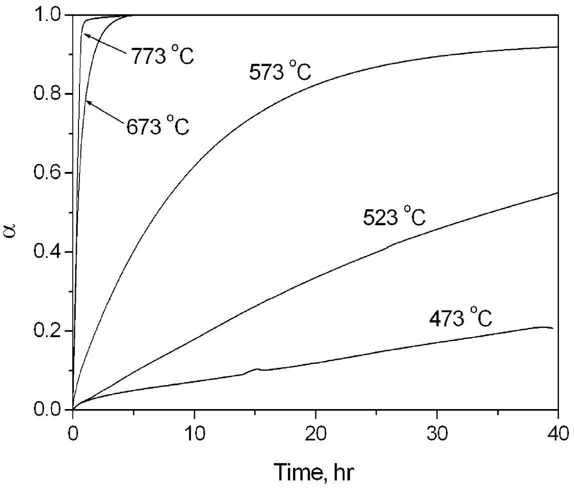

Fig. 1. Fraction reacted-time curve for the oxidation of U–10 wt% Mo in air.

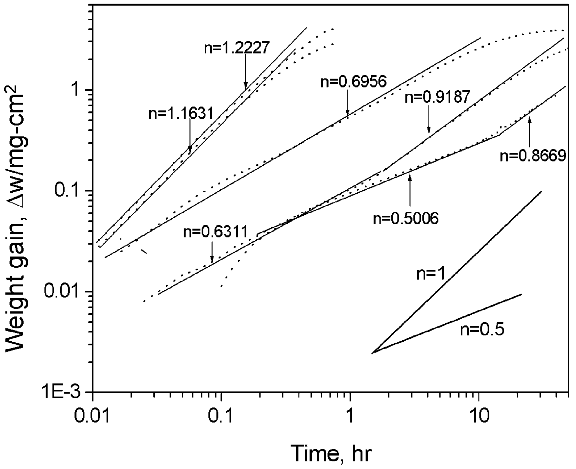

Fig. 2. Time dependence of the weight gain at 473–773 K.

At 473 and 523 K, there are two oxidation stages with transition points where the oxidation mechanism controlled by diffusion ($n \cong 0.5$) changes to that controlled by surface reaction ($n \cong 1$). The fact might be caused by that during the first oxidation process, oxygen gas diffuses through the oxide layer formed at the uranium surface before the oxidation test and after the first oxidation process oxygen gas chemically reacts with fresh surface appearing due to cracking of oxide formed at the metal surface because of density difference between uranium oxides and pure uranium. This result is in good agreement with the result from Loriers [1]. He reported that the initial layer of oxide grew and cracked up during oxidation of uranium. At 573 K, the diffusion and chemical surface reaction of oxygen gas simultaneously progress because of high diffusion rate of oxygen. Above 673 K, on the other hand, the surface reaction mechanism is predominant since the formation rate of fresh surface of uranium is higher. This result is in agreement with the result from Matsui and Yamada [13,14]. They reported that the oxidation kinetics in U–Zr alloys were able to be analyzed by a linear equation in the middle and high temperature regions (643–1063 K). Our results, however, are different from their results in the low temperature ranges (473 and 523 K). They reported that the oxidation kinetics were expressed by an equation which had a constant value of n at constant temperature.

The weight gain per unit time and area at 20% weight gain against the inverse of temperature is plotted and shown in Fig. 3. With an Arrhenius type of expression for the rate equation, the frequency factor and activation energy were calculated.

The activation energy for oxidation of U–10 wt% Mo was (66.64 ± 4.39) kJ/mol in the temperature range of 473–773 K. Kang et al. [11] reported that the activation energy for the oxidation of U_3Si was (69.65 ± 4.07) kJ/mol in the temperature range of 573–673 K and that for the oxidation of uranium was (57.46 ± 2.17) kJ/mol in the temperature range of 573–773 K, which was calculated using the values from Baker and Bingle [4].

The oxidation rate of U–10 wt% Mo is lower than that of uranium and U_3Si. The activation energy U–10 wt% Mo is similar to that of U_3Si which is, however, higher than that of uranium. Those results are similar to Antill and Peakall's results [9] in which additions of titanium, molybdenum, niobium and copper to uranium could reduce the attack in air. In this study, the reaction rate per unit time and area could be expressed as follows:

$$\mathrm{d}w/\mathrm{d}t = 5.80 \times 10^4 \exp\left(\frac{-66.64 \pm 4.39\ \mathrm{kJ/mol}}{RT}\right)$$
$$\mathrm{mg/cm^2\ min}\ (473 \leqslant T(K) \leqslant 773), \qquad (2)$$

where w, t and T are weight gain, time and temperature, respectively.

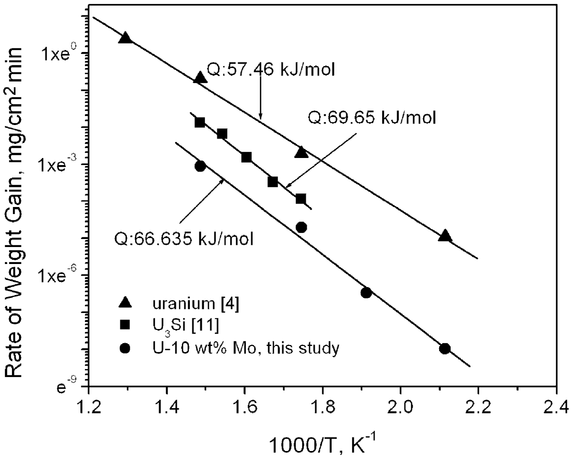

Fig. 3. Rate of weight gain versus 1000/T.

4. Conclusion

Analyses of XRD patterns and thermogravimetry in order to observe the oxidation behavior of U–10 wt% Mo have been carried out and the following conclusions are made.

(1) U–10 wt% Mo alloy after oxidation is converted to U_3O_8 at temperatures above 673.

(2) At 573 K, the diffusion and chemical surface reaction of oxygen gas progress simultaneously and above 673 K, surface reaction mechanism is predominant.

(3) The oxidation rate of U–10 wt% Mo is lower than that of uranium.

(4) The activation energy for oxidation of U–10 wt% Mo, (66.64 ± 4.39) kJ/mol in the temperature range of 473–773 K, is slightly higher than that of uranium.

Acknowledgements

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