Oxidation Behavior of UO$_2$-Mo Composite Pellets

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1. Introduction

UO$_2$-Mo composite pellets are being developed as a promising candidate for an accident tolerant fuel pellet for light water reactors in KAERI. Herein, we conduct the thermodynamic calculation to predict the equilibrium products of UO$_2$-Mo-Zr system when the system is exposed to steam or oxygen. We also examine the oxidation behavior of UO$_2$-Mo under flowing steam and air to understand the fuel degradation mechanism in the event of a steam ingress through cracks in cladding and an air contact in accident scenario.

2. Prediction of Equilibrium Products

Thermodynamic calculation of the equilibrium phase as a function of steam or air supply is expected to provide information regarding the most favorable pathway for oxidation. Thus, the changes in the Gibbs free energy for oxidation reactions of UO$_2$-Mo-Zr system in steam and air are used to predict the equilibrium products.

The equilibrium phases and their composition both at the intermediate and final stages of oxidation for UO$_2$-Mo-Zr system were calculated as a function of steam (H$_2$O) and oxygen (O$_2$) concentration and temperature using the Gem module in HSC Chemistry 9, which uses the inbuilt Gibbs energy minimization method.

Fig. 1 (a) shows the obtained diagrams for steam oxidation at 1200 °C. The ZrO$_2$ phase is preferentially formed by the reaction of Zr cladding with steam. After Zr is fully oxidized to ZrO$_2$, Mo begins to oxidize to MoO$_3$. The reaction ends with the formation of ZrO$_2$ and MoO$_3$ and UO$_2$ does not change in these temperatures and oxygen potentials.

Fig. 1 (b) shows the equilibrium phases and their compositional variation for UO$_2$-Mo-Zr system and oxygen mixtures as a function of O$_2$ content at 1200 °C. The oxidation processes of Zr and Mo to form ZrO$_2$ and MoO$_3$ are nearly identical in both steam and oxygen. However, in oxygen, UO$_2$ is further oxidized to U$_3$O$_8$ owing to the higher oxygen potential of oxygen. The subsequent oxidation reaction of UO$_2$ to U$_3$O$_8$ is possible when oxidation of Zr and Mo to ZrO$_2$ MoO$_3$ is completed under equilibrium conditions.

2. Experiments

The UO$_2$-3vol% Mo composite pellets for oxidation test were prepared by conventional sintering process. The pellet dimension is similar to that of nuclear fuel pellet. The air oxidation behavior was investigated at 450 °C in air gas atmosphere by using TGA. Steam oxidation tests were performed in an electrical tube furnace at various temperature. The samples were placed in Al$_2$O$_3$ crucibles and then heated to the target temperature in an Ar atmosphere at a heating rate of ~20 K/min. When the furnace temperature was stable, the gas was changed to steam and Ar gas mixture. Then, approximately 1.8 cc/min of distilled water was injected into a steam generator to produce steam mixed with Ar (~40 cc/min), which was supplied to the furnace. All the samples were annealed for 5 h. After annealing, the samples were cooled to room temperature in an Ar atmosphere. The weight gain was calculated by measuring the weight change of the sample before and after annealing.

Phase analysis of the samples was performed using XRD (Rigaku Ultima IV) with Cu-Kα radiation. The morphology changes of the samples after oxidation test were characterized by optical microscopy and SEM (Tescan Vega3) with an attached EDS system (Oxford Instruments, Inca X-act). During the SEM investigation, EDS was used for elemental analysis using the analysis procedure provided in the AZtec software (Oxford Instruments).

![Equilibrium products and contents for isothermal annealing of UO2-Mo-Zr system as functions of steam (a) and oxygen (b) supply at 1200 °C.](image-url)
3. Results

3.1. Air Oxidation

After the air oxidation, pellet was pulverized to small particles because of the volume expansion accompanied by the formation of U$_3$O$_8$. Fig. 2 shows the particle morphology of the sample after the oxidation. The bright particles are U$_3$O$_8$ and dark plates are partially oxidized Mo. Thermodynamic calculation in Fig. 1(b) predicts the preferential formation of MoO$_3$. However, experimental results showed the preferential oxidation of UO$_2$. This result indicates that kinetic aspect is important to address the oxidation behavior of the UO$_2$-Mo composite.

3.2. Steam Oxidation

Fig. 3(a) shows the optical image obtained at the periphery of sample pellet after the steam oxidation at 1000 $^\circ$C. Spallation of grains at pellet surface and partial oxidation of Mo plate are observed. Fig. 3(b) shows the morphology of collected particle split from the pellet. The powder consists of needle-shaped agglomerates, equi-axed small grains and lumps of grains. EDS analysis for the particles reveals that needles are Mo oxides, equi-axed grains and lump of grains are uranium oxides. XRD patterns of Fig 3(c) for collected particle confirms the presence of three phases of UO$_2$, MoO$_2$(MoO$_3$) and U$_3$O$_8$. It is anticipated that when the UO$_2$-Mo pellet is exposed to steam, the Mo at the periphery directly contacts and reacts with oxygen to form Mo oxides. Then owing to the volume expansion of Mo, the cracks may be developed and spallation occurs at the periphery. The Mo split from the pellet reacts with oxygen to form MoO$_2$ having low vapor-pressure.

Compared to the oxidation of pure UO$_2$ pellet, the UO$_2$-Mo composite showed enhanced structural stability in steam environment. It seems that Mo acts as an oxygen absorber to delay the reaction of UO$_2$ with oxygen.

4. Summary

We are studying oxidation behavior of UO$_2$-Mo pellet at various conditions to access fuel safety in normal and accident condition. It is confirmed that kinetic parameters along with thermodynamic stability is important to understand the oxidation behavior of this composite. Further detailed studies are currently underway.

ACKNOWLEDGEMENT

This work was supported by the NRF funded by Korean government (MSIP) (No. 2017M2A8A8A015056)