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_2O) and oxygen (O_2) concentration and temperature using the Gem module in HSC Chemistry 9, which uses the inbuilt Gibbs energy minimization method.

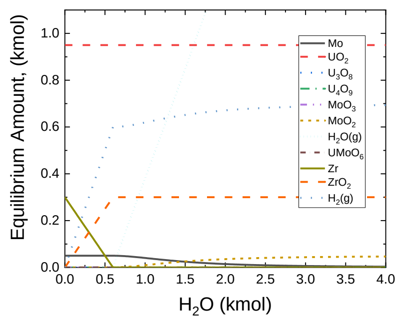
Figs. 1 (a) shows the obtained diagrams for steam oxidation at 1200 °C. The ZrO_2 phase is preferentially formed by the reaction of Zr cladding with steam. After Zr is fully oxidized to ZrO_2, Mo begins to oxidize to MoO_3. The oxidation reaction ends with the formation of ZrO_2 and MoO_3 and UO_2 does not change in these temperatures and oxygen potentials.

Figs. 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_3O_8 owing to the higher oxygen potential of oxygen. The subsequent oxidation reaction of UO_2 to U_3O_8 is possible when oxidation of Zr and Mo to ZrO_2 MoO_3 is completed under equilibrium conditions.

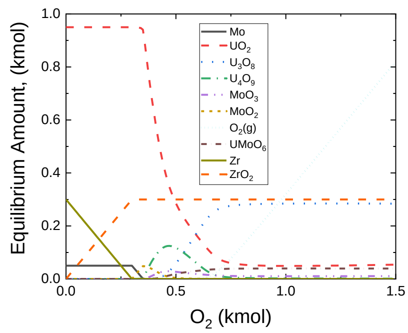
2. Experimentals

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_2O_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 microscope 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).



(a)



(b)

Fig. 1. Equilibrium products and contents for isothermal annealing of UO2-Mo-Zr systme as functions of steam (a) and oxygen (b) supply at 1200 °C.

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_3O_8. Fig. 2 shows the particle morphology of the sample after the oxidation. The bright particles are U_3O_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.

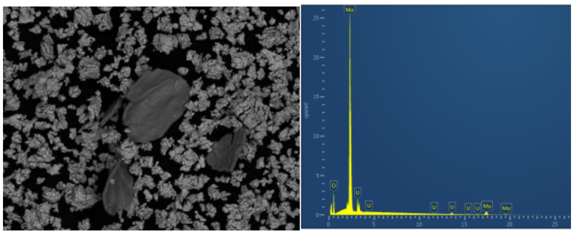
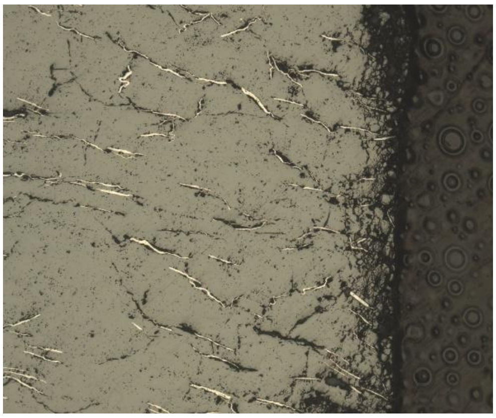
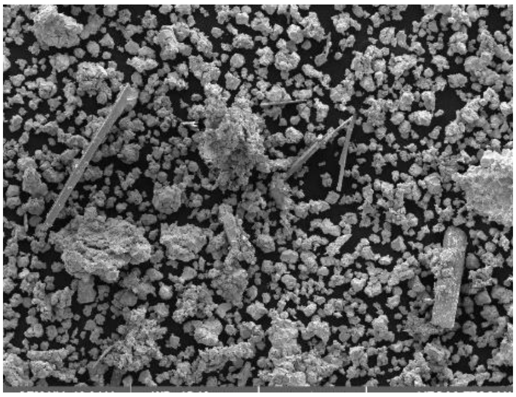


Fig. 2. SEM morphology of oxidized sample and EDS point spectrum obtained at dark plates

3.2. Steam Oxidation



(a)



(b)

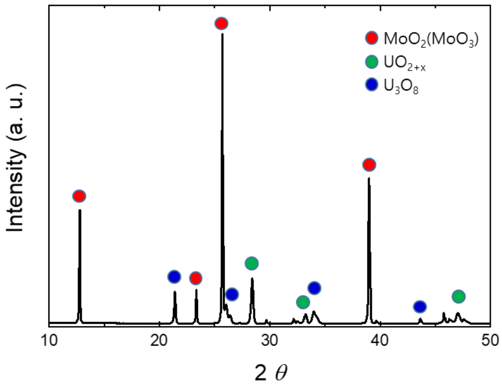


Fig. 3. (a) Optical image of post-oxidation sample. (b) SEM morphology of split powder. (c) XRD pattern of split powder

Fig. 3(a) shows the optical image obtained at the periphery of sample pellet after the steam oxidation at 1000 °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_3O_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 s 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

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