

High temperature reactions of UO_2 , ZrO_2 , B_4C , CaO , and SiO_2 under reducing and oxidizing atmospheres

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Introduction

Uranium and several other radioactive materials reacted with zircaloy(Zry) and/or its oxide, ZrO_2 , presented in the fuel cladding, to form fuel debris at the Fukushima Daiichi Nuclear Power Station in 2011. Under very high temperature conditions, the melt core, mainly consisting of the control rods (stainless steel rod filled with B_4C) and fuel assembly (UO_2 and Zry) materials, was solidified at the lower head of the pressure vessel. In addition, the melt core was also solidified at the lower head of the pedestal reacted with cement materials (CaO and SiO_2). In order to forward a safe and controlled decommissioning process, structural and thermodynamic estimations of the fuel debris under various atmospheric conditions such as reducing and oxidizing atmospheres have been conducted¹⁻². In the present study, the local structure of basic uranium/zirconium compounds has been characterized in different oxidation states and under treatment in the presence of B_4C , CaO and SiO_2 with different temperatures ranging from 1473 to 1873 K. These reactions are of specific interest to the interaction between nuclear fuel and cladding tube materials.

Results and Discussion

The uranium and zirconium compounds were characterised by powder X-ray diffraction and XAFS at the U-L_{III} edge and Zr-K edge. XAFS measurements were performed in transmission mode at BL01B1, SPring-8, Japan, using Si(311) double crystal monochromator. A suite of principal component analysis including target transformation and iterative target transformation was performed both on the acquired XANES and EXAFS spectra using the program code ITFA developed by Rossberg³. The XAFS measurements of UO_2 and ZrO_2 mixtures, treated at temperatures from 1473 to 1873 K under an oxidizing atmosphere ($\text{Ar} + 2\% \text{O}_2$), indicated that $\text{U}_2\text{Zr}_5\text{O}_{15}$ formations occurred < 1573 K, whereas UO_2 was the main product at temperatures > 1773 K. In the absence of ZrO_2 , UO_2 was oxidized to U_3O_8 indicating that UO_2 was stabilized by the formation of solid solution of $\text{Zr}_y\text{U}_{1-y}\text{O}_2$. Formation equilibrium between UO_2 and UB_4 was observed under a reducing atmosphere ($\text{Ar} + 10\% \text{H}_2$) from 1473 to 1873K. However, when ZrO_2 was present within mixtures along with UO_2 and B_4C , it was found that Zr was more reactive than U by forming ZrB_2 at 1773 K. The inclusion of CaO in a mixture with UO_2 under an oxidizing atmosphere resulted in the formation of CaUO_4 . Solid solution was the main product of the CaO and UO_2 mixture under a reducing atmosphere and then CaZrO_3 was formed in the CaO , UO_2 and ZrO_2 mixtures. This investigation shows a potential way to understanding the interaction between the nuclear fuels and the cladding materials enabling to examine possible decontamination procedures.

References

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