The Effect of Molybdenum on the Uranium Dioxide Microstructure

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1. Introduction

Uranium dioxide has been investigated continuously because of its use as a nuclear fuel. At present, several R&D programs were carried out to increase the burnup of a fuel. This burnup extension causes an increase of fission products inside the fuel. The fission products were classified by four groups. One of the groups forms solid solutions with UO_2, and another group of fission products precipitates into UO_2 matrix. Molybdenum belongs to both groups, and this special property cause the non-uniform distribution in a fuel. The state of molybdenum phase in a spent nuclear fuel is our main concern in this work.

2. Experimental

Mixed oxide of uranium and molybdenum as an additive cation was prepared by powder mixing technique, which is most widely used for the preparation of ceramic samples. The mixed oxide specimens were prepared from U_3O_8 and molybdenum dioxide powder (Aldrich, 99%). To raise homogeneity, the weighed powders were mixed well and were ground for 30 minutes to provide a small particle size and to maximize contact area of two components. The compositions of prepared pellets were listed in Table 1. The mixed powders were compacted at 2 ton for 15 seconds, and were sintered in a tubular furnace for 12 hours at 1700 ℃ and then annealed for 12 hours at 1200 ℃ under hydrogen atmosphere.

Table 1. Compositions of $U_{1-y}Mo_yO_2$ mixed oxides.

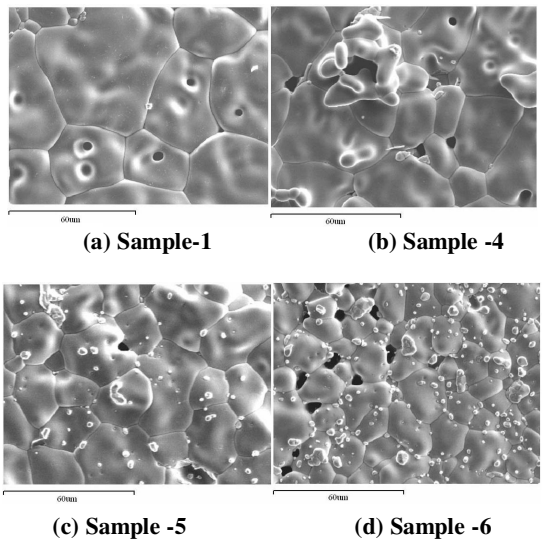
Sample	U, atom %	Mo, atom %
1	1.00	0.00
2	0.99	0.01
3	0.98	0.02
4	0.96	0.04
5	0.92	0.08
6	0.85	0.15

Visual inspection of the prepared pellets and the compositional analysis of a point were performed by electron probe micro analysis (EPMA). To get a information about structural changes of UO_2, X-ray diffraction spectra were obtained in the range of 2Θ value from 20 to 90° by Siemens D5000 X-ray diffraction (XRD) system.

3. Results and Discussions

3.1 EPMA analysis of sintered mixed oxide pellets

Visual inspection of the prepared pellets and the compositional analysis were performed by EPMA to understand microstructure transformation of UO_2 by molybdenum. The pellets revealed homogeneity of Mo distribution for lower content, while those revealed heterogeneity by precipitates for higher content. Fig. 1 shows the changes of morphology with respect to Mo content. From the microstructures, we could see that the distribution of Mo is heterogeneous within micro region. Table 2 listed the changes of $U_{1-y}Mo_yO_2$ mixed oxides composition within a square of a few tens of micrometers in each side.



(a) Sample-1 **(b) Sample -4**

(c) Sample -5 **(d) Sample -6**

Figure 1. The changes of morphology with respect to Mo content: (a) UO_2, (b) $U_{0.96}Mo_{0.04}O_2$, (c) $U_{0.92}Mo_{0.08}O_2$ and (d) $U_{0.85}Mo_{0.15}O_2$.

Table 2. The compositions of mixed oxides, $U_{1-y}Mo_yO_2$ analyzed by EPMA

element / sample	O at. %	U at. %	Mo at. %
1	74.59	25.41	-
2	75.13	24.48	0.39
3	76.08	22.01	1.91
4	75.38	23.42	1.20
5	72.27	23.11	4.62
6	71.53	21.51	7.32

3.2 The changes of lattice parameter by XRD spectra

To observe the doping effect of Mo into UO_2 lattice, powder XRD was performed. In U-Mo mixed oxides, lattice parameter was increased as the increase of Mo content due to the ion radii of Mo as reported by others[1,2]. However, it became to decrease when Mo content was above 4 atom % (y > ca. 0.04). At this composition, the XRD patterns revealed phase separation of Mo metal from the mixed oxide. Therefore, the lattice decrease can be explained by the formation of metal precipitates in UO_2 matrix. The results agreed well with that of EPMA analysis.

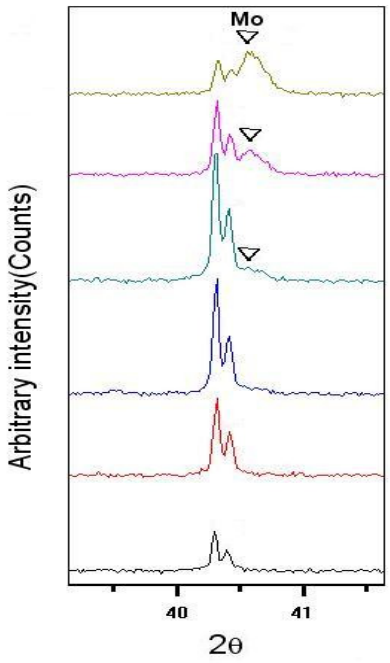


Figure 2. The X-ray diffraction patterns of $U_{1-y}Mo_yO_2$ mixed oxides. (y : 0, 0.01, 0.02, 0.04, 0.08 and 0.15 from bottom to top, respectively)

4. Conclusion

The effect of molybdenum cation on uranium dioxide structure was studied by EPMA and XRD. The following was concluded.

1) The addition of Mo influence lattice structure of uranium dioxide due to the ion radii and charge, leading to lattice expansion until the Mo content reach ca. 4 atom % of metal cation.
2) Mo starts to precipitate in UO_2 matrix at above 4 % Mo, resulted in lattice contraction.
3) Mo exists as a solid solution and also as a metallic precipitate in UO_2 matrix depending on its content. This means that the distribution of Mo could be heterogeneous throughout the UO_2 matrix at high burnups.

Acknowledgements

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