Separation of Thorium and Uranium by Sulfide Method

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Abstract

For the recovery of nuclear materials from spent fuel, a novel reprocessing process based on sulfide chemistry has been proposed. In this paper, the sulfurization behavior of thorium and uranium oxides was studied using carbon disulfide. When U₃O₈ was reacted with CS₂, it was reduced to UO₂ at temperatures lower than 673 K, while sulfurization of UO₂ was observed at temperatures higher than 773 K forming UOS and US₂. On the other hand, no reaction was observed for ThO₂ up to 773 K. Similar results were obtained for the mixture of U₃O₈ and ThO₂. The obtained results were also compared with thermodynamic consideration. Then, separation of uranium from thorium was suggested by selective sulfurization of uranium oxides. Finally, it was summarized that most of thorium oxide could be recovered as ThO₂ after the separation of sulfurized uranium oxides.

Keywords: Spent fuel; uranium; thorium; sulfurization

1. Introduction

For the recovery of uranium from spent nuclear fuel, we have proposed the sulfide reprocessing process. In this process, voloxidation for decladding and sulfurization for FP separation are applied to the UO₂ spent fuel (Ref. 1). When UO₂ was oxidized to U₃O₈, some of the fission products, such as rare-earth elements formed solid solution with UO₂ at 1273 K. Then the sulfurization of the solid solution phase was examined at temperatures lower than 773 K. In our previous report (Ref. 2), U₃O₈ was reduced to UO₂ by the sulfurization using CS₂ at temperatures lower than 773 K, while rare-earth oxides were easily sulfurized forming oxysulfides and sulfides.

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Then the sulfirized rare-earths were separated from the uranium oxides by the selective dissolution using nitric acid. Furthermore, it was also suggested that plutonium would show similar behavior to uranium by the simulated experiment using CeO₂ as PuO₂ (Ref. 3). Behavior of the minor actinides such as neptunium and americium were investigated by the sulfurization as dissolution experiments using their tracers. Finally, a novel reprocessing process based on sulfide chemistry has been proposed. This process could be applicable to the thorium fuel cycle. In this paper, separation of thorium and uranium by the sulfide method was discussed.

2. Experimental

2.1. Sample Preparation

The U₃O₈ sample was obtained by the oxidation of U metal turnings in air at 1073 K. Stoichiometric UO₂ was prepared by the H₂ reduction of U₃O₈ at 1273 K. The ThO₂ powder was used without further purification. Analytical grade CS₂ with a boiling point of 46-47 °C and maximum water content of 0.02% (Wako Pure Chemicals Co., Ltd.) and Argon gas of 99.99% purity (Nippon Sanso Co., Ltd.) were used as received.

2.2. Sulfurization Experiments

Sulfurization experiments were carried out by using the quartz apparatus as shown in Fig. 1. After the weighed sample was placed on the quartz boat in a quartz tube, the reaction system was evacuated by rotary pump followed by refilling with argon. Then the temperature of the furnace was raised to an intended temperature at a heating rate of 10 K/min with a CS₂/N₂ gas flow rate of 5/50 ml min⁻¹. The N₂ gas flow rate was measured using a digital mass flow meter (Kofloc Model DPM-2A). After the sulfurization, the phase analysis of the sample was conducted by powder X-ray diffraction method.

![Fig. 1 Schematic drawing of sulfurization apparatus.](image)

2.3. Analysis

For the phase analysis of the products, the X-ray powder diffraction was carried out with a Rigaku Type RAD-IC diffractometer using CuKα radiation (40kV, 20mA) monochromatized by curved pyrolytic graphite. The slit system was 1.0°-1.0°-0.3mm-0.6mm. The measurement was performed from 2θ = 10 to 100° by continuous scanning with an interval of 0.02°. The phase of the product was identified by comparing the obtained data with that of JCPDS.

3. Results and discussions

3.1. Thermodynamic consideration

In order to know the thermodynamic stability of the compounds in the presence of sulfur and oxygen, a potential diagram of the M-O₂-S₂ system (M= U and Th) at 773 K was constructed using the DATABASE MALT for Windows (Ref.4). The result of uranium is shown in Fig. 2. The SO₂, CS₂ and CO₂ of 1 atm are also given in the figure as dotted lines. The stable sulfides are US, U₃S₄, U₂S₃, US₂ and US₅. The stable oxides are UO₂, U₄O₉, U₃O₈ and UO₃. In the figure, the areas of UO₂SO₄ and U(SO₄)₂ are located above the oxides and sulfides. The UOS phase appears at the boundary between the oxides and sulfides. When U₃O₈ react with 1 atm CS₂ gas at SO₂ pressure of 1 atm, formation of US₅ proceed via U₄O₉ along the dotted line. However, formation of UO₂SO₄ and UOS would occur if the CS₂ and SO₂ pressures change in the experiments. In the case of uranium recovery cycle, sulfurization of uranium is suppressed, that of rare-earth oxides is promoted.
The stability diagram for the Th-O$_2$-S$_2$ system is shown in Fig. 3. Three sulfides, ThS, Th$_2$S$_3$ and ThS$_2$, and one oxide ThO$_2$ appear in the figure. The oxisulfide ThOS is not given in the figure for the lack of thermodynamic data. For the comparison with the uranium, the border between UO$_2$ and UOS is also given as a dotted line in the figure. It is suggested that the small area in which UOS and ThO$_2$ are stable. The cross point (a) of equilibrium sulfur and oxygen potentials appears in the UOS region suggesting the selective sulfurization of uranium oxides.

Fig. 2 Stability diagram for the U-O$_2$-S$_2$ system at 773 K.

The stability diagram for the Th-O$_2$-S$_2$ system is shown in Fig. 3. Three sulfides, ThS, Th$_2$S$_3$ and ThS$_2$, and one oxide ThO$_2$ appear in the figure. The oxisulfide ThOS is not given in the figure for the lack of thermodynamic data. For the comparison with the uranium, the border between UO$_2$ and UOS is also given as a dotted line in the figure. It is suggested that the small area in which UOS and ThO$_2$ are stable. The cross point (a) of equilibrium sulfur and oxygen potentials appears in the UOS region suggesting the selective sulfurization of uranium oxides.

Fig. 3 Stability diagram for the Th-O$_2$-S$_2$ system at 773 K.
Free energy for the sulfurization of ThO$_2$ and UO$_2$ with CS$_2$ is shown in Fig. 4. It is seen that sulfurization of UO$_2$ occurs first at low temperatures, while that of ThO$_2$ may not occur. From these results, it is suggested that the selective sulfurization of UO$_2$ in the UO$_2$-ThO$_2$ mixture is possible.

![Fig. 4 Gibbs free energy for the sulfurization of ThO$_2$ and UO$_2$ with CS$_2$.](image)

3.2. Sulfurization behavior of ThO$_2$ with CS$_2$

To examine the sulfurization behavior of ThO$_2$ with CS$_2$, the ThO$_2$ powders was heat-treated in CS$_2$ for 1 hour at different temperatures. The XRD result of the product obtained at 773 K was given in Fig. 5 (b). The XRD data for the starting material is also given in the figure for comparison (a). The peaks of starting material correspond to the that for the fluorite structure. From the results, it is seen that the pattern of the ThO$_2$ after the sulfurization is the same as that of starting material. This suggests that ThO$_2$ is stable up to 773 K in the presence of CS$_2$.

![Fig. 5 XRD result of the ThO$_2$ after the reaction with CS$_2$ at 773 K for 1 hr.](image)

Next, the sulfurization behavior of UO$_2$ with CS$_2$ was examined and compared with that of the ThO$_2$. In the experiment, UO$_2$ powder was heat-treated in CS$_2$ for 1 hour at 773 K. The dark brown color of UO$_2$ was changed to black after the reaction. The XRD result of the product was given in Fig. 6 (b). The XRD data for the starting material is also given in the figure for comparison (a). The peaks of starting material correspond well to that for the
UO$_2$ fluorite structure. From the result of Fig. 6 (b), the peaks of the UO$_2$ structure were observed even after the sulfurization. However, small peaks correspond to the UOS phase appear in Fig. 6(b). This suggests that UO$_2$ is partially sulfurized by CS$_2$ at 773 K forming UOS.

4. Conclusions

In this paper, sulfurization behavior of thorium and uranium dioxides with CS$_2$ was investigated by thermodynamic consideration using MALT program and phase analysis using powder XRD method. The obtained results are summarized as follows;

- From the thermodynamic consideration, selective sulfurization of UO$_2$ in the UO$_2$-ThO$_2$ mixture seems to occur by the reaction of the mixture with CS$_2$ at 773 K.
- Thorium dioxide was found to be stable up to 773 K in the presence of CS$_2$.
- By the reaction of UO$_2$ with CS$_2$ at 773 K, part of UO$_2$ was sulfurized forming UOS.

References