Advanced Nuclear Fuel Cycle Train Program in Tohoku University: Experiments on Solid States and Solution Chemistry

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1. Introduction

In this experimental study program in Tohoku University, there are four experiment related with nuclear fuel cycle. First one is the oxidation and reduction process of UO_2. Second one is to observe microscopic structure of solid solution of UO_2 and ZrO_2 using SEM/EDX and XRD system. Third one is milking process of 239Np from 243Am by solvent extraction using Tri-n-Octylamine (TOA). Last one is solvent extraction in PUREX by the simulated mixed aqueous solution of U, 85Sr and 239Np which is represented minor actinide elements included in the spent nuclear fuel.

2. Experiment procedure

2.1 Procedure of UO_2 Oxidation and Reduction

We conducted two experiment. First, we did experiment which is related about the transition of UO_2 by heating it up. The process is reduction and oxidation (REDOX). After heat treatment. We used XRD to analyze the structure of material. second we used TG-DTA to analyze weight gain and enthalpy of each reaction.

2.2 Procedure of solid solution $Zr_yU_{1-y}O_2$ (y = 0.05 and 0.1)

We did experiment which is related about the Formation of Solid Solution $Zr_yU_{1-y}O_2$. Heating up the temperature from R.T to 1400℃ using Ar + 10% H_2 gas. In this experiment, we investigate the morphology of $Zr_yU_{1-y}O_2$ by scanning electron microscopy (SEM). In addition, the structure change by the formation of solid solution were examined using X-ray diffraction (XRD).

2.3 Procedure of milking process for extraction of Np-239

The procedure of experiment for milking process can be divided into four stages. The first step is to make the pre-equilibrium. The second step is a extraction of Np239 to organic phase. The third step is Stripping process, which is back extraction of Np to aqueous phase. The final step is fuming of Np239 solution.

2.4 Procedure of extraction of uranium in the solution that Contains Np-239 and Sr-85

In this study, we are focusing on the behavior of MAs and FPs during the solvent extraction. 239Np is a MAs and it is extracted with U and Pu in some conditions. so we using 3 different solution containig U, 239Np, 85Sr. and Solution has various nitric acid concentration as 0.1M, 1.0M, 5.0M, the separation factor is affected by the nitric acid concentration so we calculated the separation factor and find best condition for the extraction of Uranium only, from aqueous phase containig 239Np and 85Sr.

3. Result and discussion

3.1 Result of UO_2 Oxidation and Reduction

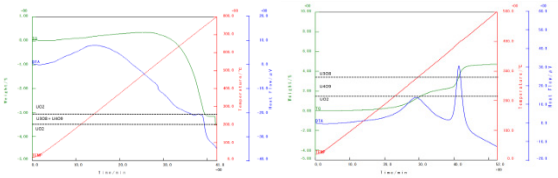

Fig. 1. TG-DTA curve of oxidation and reduction.

DTA line shows two peaks. around the black line. This peak show us its exothermic reaction during oxidation. Additionally, this two peaks and mass gradient is steeply change almost simultaneously. This peak and mass change proved phase transformation

In the reduction process, It is only once that the mass gradient changes steeply. Also, DTA line shows one exothermic peak around the black line. Theoretical mass change of U_3O_8 to U_4O_9 is -2.38wt% and mass change of U_3O_8 to UO_2 is -3.8wt%. In our experiment, there are not flat line around -2.38wt%, In fig. 4, Second flat line of TG is around -3.5wt%. Thus, reduction reaction of U_3O_8 is directly change to UO_2.

We can calculate the density of UO_2 and U_3O_8 . using the measured lattice parameter, volume of unit cell of UO_2 and U_3O_8 is 163.4879×10^{-24} cm^3 and 334.8809×10^{-24} cm^3, As a result of calculation using volume and mass of unit cell, the density of UO_2 and U_3O_8 is 10.9680 g/cm^3 and 8.3501 g/cm^3. During oxidation of UO_2, the density decreased by about 30%, which means a volume increase of about 30%.[1]

3.2 Result of solid solution $Zr_yU_{1-y}O2$ (y = 0.05 and 0.1)

According to SEM/EDX images of synthesized $Zr_yU_{1-y}O_2$ solid solution (y = 0.05, Figure 2), uranium and zirconium seem to be distributed homogeneously.

However, EDX results were $Zr_{0.0311}U_{0.09689}O_2$ and $Zr_{0.0537}U_{0.09462}O_2$ for y = 0.05 and 0.1, respectively. Determined values (0.0311 and 0.0537) by EDX were less than initial values (0.05 and 0.1). the rate limiting step in the formation of solid solution may be the self

diffusion of U in UO_2 [2]. So we need more annealing time considering self diffusion coefficient of U in UO_2 for formation of solid solution.

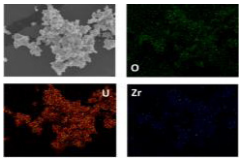

Fig. 2. Result of EDX analysis.

Fig. 2 is a result of lattice parameter. Lattice parameter of $Zr_yU_{1-y}O_2$ were 5.43458 and 5.42422 Å for y = 0.05 and 0.1. The lattice parameter had a decrease tendency as increasing Zr portion. Thus, volume of solid solution is decrease compared with UO_2. Shrinking of unit cell may be due to the intrusion of Zr

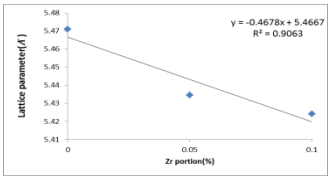

Fig. 3. Lattice parameter of solid solution.

3.3 Result of milking process for extraction of Np-239

The daughter radionuclides can be extracted from parent radionuclides persistently using milking process. For this process, the condition of secular equilibrium should be satisfied. Np239 is extracted from Am243.

During the Np extraction process, Np(IV) and Np(VI) are extracted to organic phase(Tri-Octylamine in xylene) and Am243 remains in aqueous phase(HCl). For Stripping process, the Np back extraction occurs because of the distribution ratio decreases by decreasing the concentration of HCl. Finally for fuming process, nitric acid is used for higher purification

3.4 Result of extraction of uranium in the solution that Contains Np-239 and Sr-85

$$\gamma = \frac{[U]_{org}/[U]_{aq}}{[Np]_{org}/[Np]_{aq}} \qquad (1)$$

Separation factor is calculated following equation (1). separation factor means that we can get much more purificated uranium during solvent extraction.

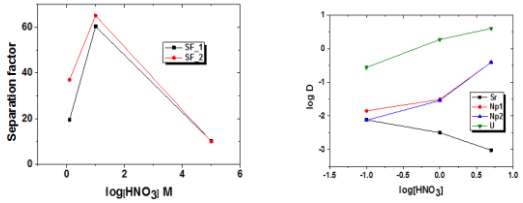

Fig. 4. Separation factor and concentration of nitric acid.

Separation factor is affected to concentration of nitric acid. In the Fig. 4. separation factor has a most high value at the 1.0M of nitric acid. so we can guess 1.0M of nitric acid is a best condition of PUREX for extract uranium without neptunium. this result means that 1.0M of nitric acid can make a high purification of uranium

4. Conclusion

In the first experiment, we are able to get the sense of phase change of uranium oxide as measuring weight from TG-DTA experiment. When UO_2 is in oxidation to U_3O_8, it has a change of structure. By using XRD, we can get the structure of UO_2,U_3O_8 and the lattice parameter of that. By using the lattice parameter, we can notice that there is a volume expansion during the oxidation process of UO_2 to U_3O_8.

In the second experiment, By using EDX, we measured a ratio of Zr and U in the solid solution . the measured ratio is less than initial value (0.05 and 0.1). The diffusion coefficient of U is much smaller than O in UO_2. So U is the rate limiting step in formation of solid solution. we need more annealing time for formation of solid solution. By using XRD, we are able to guess the effect of cation to the lattice parameter. The lattice parameter had a decrease tendency as increasing Zr. Thus Shrinking of unit cell may be due to the intrusion of Zr.

In the third experiment, extraction of Np239 using the milking process is analyzed during the experiment. The chemical reactions are derived during this process. After a series of steps using the TOA. We can get the Np239 from Am234.

At last one, To determined the best condition of PUREX for a high quality of uranium, Neptunium has a low distribution coefficient. as increasing concentration of nitric acid. Neptunium exist Np (IV) and Np (VI) dominant, It make that distribution coefficient is increased. In this study, the best condition for PUREX process is 1.0M of nitric acid. To get more value, need more experiment as a various concentration of nitric acid.

5. Reference

[1] Reduction Kinetics of Uranium Trioxide to Uranium Dioxide Using Hydrogen Pedro Orrego Alfaro1, José Hernández Torres1, Fernando Puchi Thiele2, World Journal of Nuclear Science and Technology, 2015, 5, 149-156.

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