SEPARATION OF ZIRCONIUM FROM LiF-BeF_2-ZrF_4 MOLTEN-SALT BY PYROHYDROLYSIS

Mun-Sik Woo, Sung-Chan Hwang, Jun-Bo Shim, Young-Ho Kang and **Jae-Hyung Yoo**
Korea Atomic Energy Research Institute
Yusong P.O. Box105, Daejon City, 305-600 Korea

Abstract

In this study, zirconium was chosen as a surrogate of actinides in order to infer the separation behaviour of actinides in the pyrohydrolysis of LiF-BeF_2-ZrF_4 molten salt. The reactivities of zirconium, actinides and lanthanides in the pyrohydrolysis were predicted from their Gibbs free energies of formation (ΔG_0^f) which were calculated by using the JANAF table [1] as well as the HSC thermodynamic code. In the pyrohydrolysis experiments, ZrO_2 was formed from ZrF_4 in the salt by the reaction with steam and then the ZrO_2, precipitated at the bottom of the reactor, was recovered by vacuum distillation of the salt at the condition of $1.1\sim10^{-3}$torr and 1 000°C. The conversion rate of ZrF_4, the size distribution and shape of ZrO_2 particles, were found to depend on the various experimental parameters such as steam feeding rate, reaction temperature, and argon gas flow rate. As results, plate-type and columnar-type of ZrO_2 particles were obtained.

Introduction

A trans-uranium (TRU) fuel should be manufactured and loaded in transmutation systems in order to transmute the long-lived TRU nuclides into short-lived ones. However, since all of the TRU nuclides are not completely transmuted in one cycle lifetime in transmutation systems, the spent TRU fuel has to be treated to recover the long-lived radionuclides or fuel matrix materials. One concept to manufacture TRU fuel for transmutation is to prepare a metal-type fuel with TRU and zirconium as a fuel matrix. If this type of fuel is adopted for transmutation, zirconium could also be an objective material to be recovered and recycled. [2] Since steam pyrohydrolysis is a promising technology to be employed for the recovery of zirconium from fuel materials, some experimental work of pyrohydrolysis was carried out in this study. The basic salt chosen was a mixture of LiF-BeF_2 which has an eutectic point at 458°C.

Experimental

The pyrohydrolysis equipment used in this work is shown in Figure 1. It consists of a muffle furnace, reactor, argon gas supplying system, effluent gas collecting system, steam generator, the personal computer system and recorder. Molten salt in nickel crucible was mixed by bubbling inert argon gas. And argon gas was supplied into steam generator in order to control steam feed rate supplied to reactor. The eutectic salt LiF-BeF_2-ZrF_4 (62.3-30.7-7 mol %) was prepared, 19.5g per batch, at 500°C. Ammonium fluorides were added in order to fluorinate the trace oxides in the initial fluorine materials. The experimental conditions are shown in Table 1. The reactivities of zirconium, actinides and lanthanides in the pyrohydrolysis were predicted from their Gibbs free energies of formation (ΔG_0^f) which were calculated by using the JANAF table as well as the HSC thermodynamic code. The precipitate of ZrO_2 after pyrohydrolysis was recovered by vacuum distillation of the salt at the condition of 1.1~10^{-3}torr and 1 000°C. The chemical analyses were done by using a particle analyser (PA), x-ray diffractoneter (XRD) and a Scanning electron microscope (SEM).

Table 1. **Experimental conditions for pyrohydrolysis of ZrF_4**

Experimental No.	**Temp.** (°C)	**Steam feed rate** (mL-H_2O/h)	**Reaction time** (hour)	**Ar-gas flow rate** (mL/min)	**Cooling time** (hour)
Run 1	500, 600, 700, 800, 900	1.3	3	100	4
Run 2	600	1.3, 5.7, 7.3, 16.7	3	100	2
Run 3	600	1.3	1, 2, 3, 5, 10	100	4
Run 4	600	1.3	3	0, 30, 70, 100, 150	4
Run 5	600	1.3	3	100	1, 2, 4, 7, 10

Results and discussion

The results of the calculation on reactivities of zirconium, actinides and lanthanides in the steam pyrohydrolysis with temperature were predicted from their Gibbs free energies of formation (ΔG_0^f) as Figures 2 and 3. The results given in Figures 2 and 3 indicated that each element can be separated by the difference of reaction temperature in the steam pyrohydrolysis.

Figure 1. **Schematic diagram of apparatus for pyrohydrolysis**

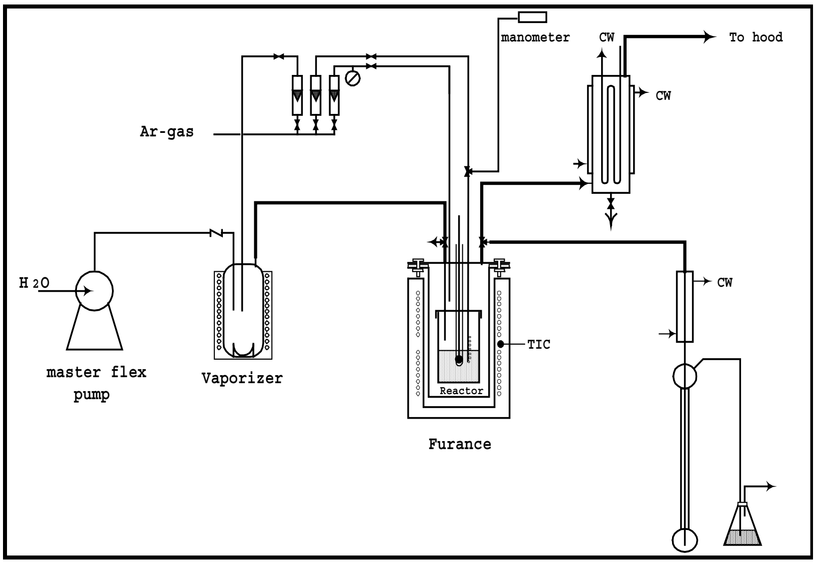


Figure 2. **Gibb's free energies of formation of various compounds**

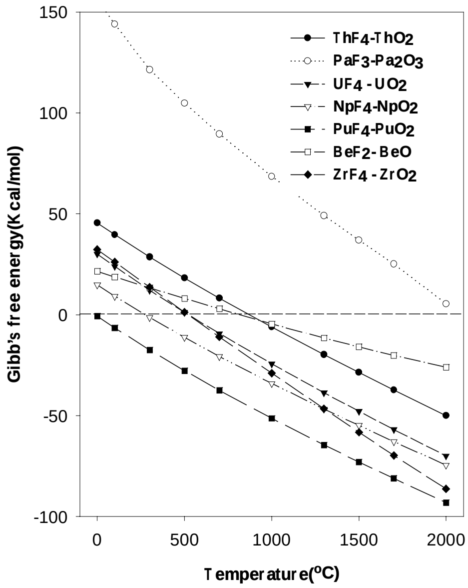
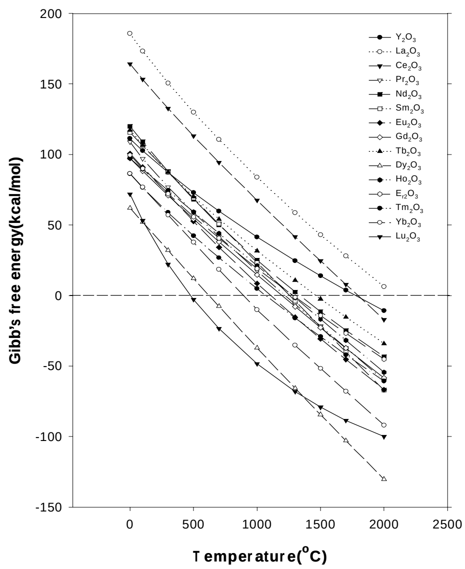


Figure 3. **Gibb's free energies of formation of lanthanide fluorides**



In the pyrohydrolysis experiments, ZrO_2 was formed from ZrF_4 in the salt by the reaction with steam at various experimental parameters as in Table 1. The results of the experimental are as follows: (as shown Figure 4) conversion rate of ZrF_4 reacted with steam for 3 hours at 550°C, was about 99wt% and, in general, was increased with increased temperature, concentration of steam, reaction time, mixing velocity. Though, as in Figure 5, the conversion rate was increased with temperature up to 800°C, it was rather decreased at 900°C due to the volatility of ZrF_4. The mean particle size of ZrO_2 was increases up to 70 μm with increased temperature and cooling time. as shown in Figure 6. The assay result of XRD on precipitated ZrO_2 was pure ZrO_2 materials as in Figure 7. Plate-type and columnar-type of ZrO_2 particles were obtained when difference of temperature between steam and salt was large, as shown in Figure 8.

Figure 4. **The conversion ratio of ZrF_4 vs. reaction time**

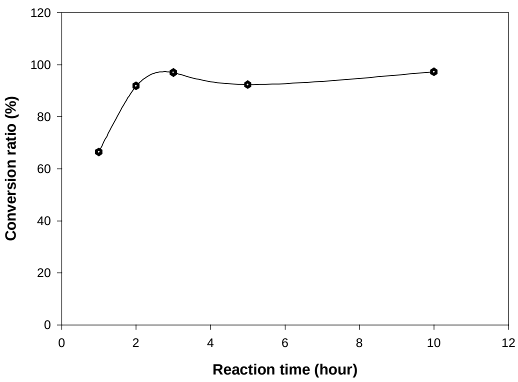


Figure 5. **The conversion ratio of ZrF_4 vs. reaction temperature**

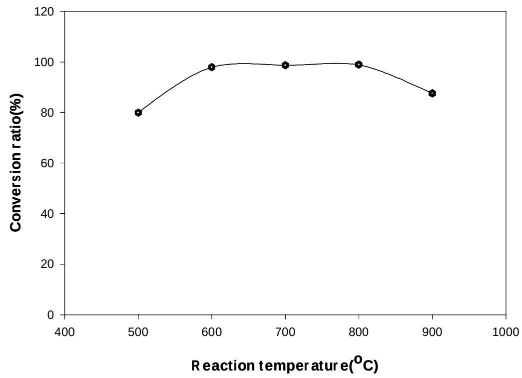


Figure 6. **Plots of mean particle size of ZrO_2 vs. temperature**

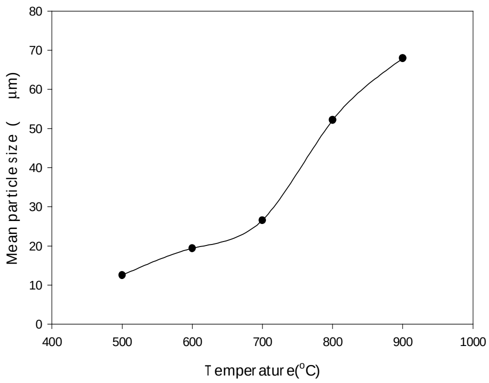


Figure 7. **XRD patterns of ZrO_2 formed by pyrohydrolysis**

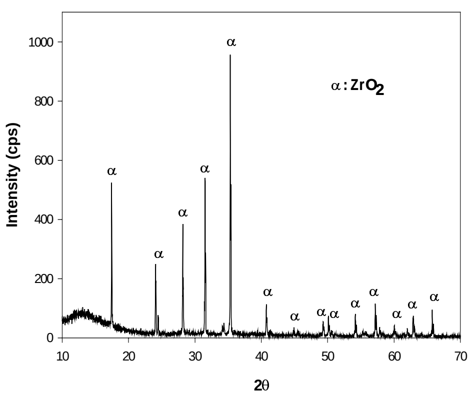


Figure 8. **SEM photographs of ZrO_2 formed by pyrohydrolysis conclusion**

The fundamental experimental results obtained in this study show that each elements can be separated by the difference of reaction temperature in the steam pyrohydrolysis. In addition, it may be required to do more study in order to completely develop the separation process by pyrohydrolysis.

Acknowledgement

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REFERENCES

[1] D.R. Stull, H. Prophet (1971), *JANAF Thermochemical Tables*, 2nd ed. NSRDS-NBS37.

[2] M.E.Whatley, L.E. McNeese *et al.* (1970), Nucl. Appl. Technol., Vol. 8, 170-178.