Fluorination of Metals and Metal Oxides by Gas-Solid Reaction

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Received September 20, 2001; Accepted September 3, 2002

Abstract: The technology on the transmutation of nuclear waste has been developed to reduce the risks during the long-term storage of the long-lived radioactive nuclides. The fluorination of metals and metal oxides was studied to investigate the preparation of the fuel for a transmutation reactor. The solid reactants reacted with diluted hydrogen fluoride gas to produce fluorides in a monel tubular reactor. CeO2, Nd2O3, and SrO were successfully fluorinated by the gas-solid reaction method. Noble metals did not react with hydrogen fluoride gas and could be separated from other elements during the dissolution step. Among the various gas-solid reaction models, the phase boundary controlled (reaction controlled) model was suitable for the fluorination of CeO2, whereas the nucleation and growth model was suitable for Nd2O3 and SrO. Reaction time required for the complete conversion could be predicted from the models.

Keywords: fluorination, metal, metal oxide, gas-solid reaction

Introduction

There are many kinds of long-lived radionuclides in high-level radioactive wastes including spent nuclear fuels. Generally, the wastes have been stored in an interim site or repossited in a deep geological formation [1-3]. To reduce the burden of long-term risk during storage, it was proposed to separate and transmute the long-lived elements into short-lived or stable elements [1-7].

Long-lived radionuclides need to be partitioned from the high-level wastes or spent fuels to manufacture a fuel for a transmutation reactor. Partitioning processes can be classified into two categories; a wet type and a dry type. Separation is carried out using an aqueous media in the wet process, whereas molten salt is used as a separation media in the dry process. The dry process has many advantages over the wet process in compactness, reduction of secondary wastes, and reaction kinetics [5-7]. The dry process is being studied in several countries with a focus on the establishment of proliferation resistant fuel cycle technology [5,6,8]. In the dry process, electrochemical methods are used for the partitioning of the long-lived radioactive nuclides.

The fluorination process of high-level radioactive waste is an important step to produce fluoride molten salt, which is used for the subsequent electro-separation step during the manufacture of the transmutation reactor fuel. In the electrochemical separation step, long-lived radioactive nuclides are group partitioned. Fluoride molten salt can be manufactured in two ways; the fluorination of metal and metal oxides directly in the basic salt such as LiF-BeF2 (three-phase reaction), or the preparation of fluorides and dissolution of the prepared fluorides into the basic salt. The present authors reported that the gas-solid reaction method is effective for the fluorination of some oxides and is preferable to the three-phase reaction method [9,10].

Spent nuclear fuel contains various kinds of metals and metal oxides such as actinide, rare earth, noble metal, alkaline, and alkaline earth elements. Their fluorination characteristics are expected more or less to be different from each other. Rare earth elements are major components to be partitioned for the manufacture of the transmutation reactor fuel.

In this study, the fluorination behavior of some oxides and metals such as CeO2, Nd2O3, SrO, Ag, and Pd was investigated.

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Experimental

Reagents
The solid reactants were cerium dioxide (CeO₂), neodymium dioxide (Nd₂O₃), strontium oxide (SrO), silver (Ag), and palladium (Pd), supplied by Aldrich Co. Two types of CeO₂ were used; powders with an average diameter of about 1.2 μm and particles with a diameter of about 3 mm. The average diameters of Nd₂O₃ and SrO were about 1.7 and 4.5 μm, respectively. Anhydrous hydrogen fluoride (HF), high purity (>99.999%) argon and hydrogen were used as the gaseous reactants.

Experimental Set-up and Procedure
The experimental set-up was composed of a gas supply system, a gas-solid reactor system, and an off-gas treatment system, as shown in Figure 1. The gaseous reactants were supplied via a mass flow controller to the gas-solid reactor. Liquid hydrogen fluoride was vaporized and fed to a buffer tank to avoid the entrapment of the mist to the mass flow controller. Argon gas was used to dilute the hydrogen fluoride gas except for CeO₂. Hydrogen gas was used instead of argon gas in the case of CeO₂. The flow rate of hydrogen fluoride and argon or hydrogen gases were 100 and 200 mL/min, respectively. The total gas flow rate of the mixed gas was kept at 300 mL/min in all experiments. The gas-solid reactor system consisted of a tubular furnace and a gas-solid reactor. The reactor was made with a 3” diameter (schedule #80) monel alloy tube. The length of the reactor was 70 cm.

At each run, about 1 g of solid reactant contained in a 3x4 cm monel boat was placed in the center of the reactor. Then, the temperature of the reactor was slowly increased to the reaction temperature in the argon or hydrogen atmosphere. After being kept for more than 1 h at the reaction temperature, hydrogen fluoride gas was fed into the reactor. The reaction temperature was varied from 300°C to 500°C. The resulting fluoride was analyzed by X-Ray Diffractometry (XRD). The off-gases generated during the reaction were absorbed and neutralized in the off-gas treatment system, which is composed of a water bed and a KOH bed.

Analysis
The fractional conversion after the gas-solid reaction was measured by an External Standard Method of XRD analysis [10].

Results and discussion
Spent nuclear fuel contains various kinds of metals and metal oxides such as actinide, rare earth, noble metal, alkaline, and alkaline earth elements. Their fluorination behavior of metals and oxides was investigated with CeO₂, Nd₂O₃, SrO, Ag and Pd.

Fluorination of CeO₂ and Nd₂O₃
Rare earth elements are major components to be partitioned from actinides for the manufacture of the transmutation reactor fuel. CeO₂ and Nd₂O₃ were selected for the investigation of the fluorination behavior of the rare earth elements.

Generally, rare earth oxide reacts with HF to produce oxide and water as expressed in the following equation.

\[ M_{2}O_{3} + 6HF \rightarrow 2MF_{3} + 3H_{2}O \]  

where M is a rare earth element. However, the fluorination behavior of cerium oxide is different from other rare earth oxides. As expressed in the following equation, hydrogen is needed for the proceeding of the reaction and the oxides are reduced from tetra-valence to tri-valence during fluorination [10].

\[ 2CeO_{2} + 6HF + H_{2} \rightarrow 2CeF_{3} + 4H_{2}O \]  

The oxides of transuranic elements show the same manner. Therefore CeO₂ is used as a surrogate for the oxides of transuranic elements in this study.

Figure 2 shows the Gibbs free energy for the fluorination reaction of CeO₂ and Nd₂O₃. The Gibbs free energy values were calculated using a computer program (HSC Chemistry for Windows produced by Outokumpu Research Oy Information Service) [11]. Based on the Gibbs free energy for the reactions, it is expected that both oxides can be fluorinated thermodynamically over a wide range of reaction temperatures. However, considering the reaction kinetics, it is necessary to determine the optimum reaction conditions experimentally.

Figure 3 and 4 show the XRD patterns of CeO₂ and Nd₂O₃ powders, respectively, along with the resulting
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**Figure 2.** Gibbs free energy for fluorination reaction of some rare earth oxides.

**Figure 3.** XRD patterns of (a) CeO$_2$ and (b) CeF$_3$ prepared by gas-solid reaction.

**Figure 4.** XRD patterns of (a) Nd$_2$O$_3$ and (b) NdF$_3$ prepared by gas-solid reaction.

**Figure 5.** Fluorination fraction of CeO$_2$ powders with an average diameter of 1.2 µm.

**Figure 6.** Fluorination fraction of CeO$_2$ particles with an average diameter of 3 mm.

Fluorides prepared by the fluorination at 300°C during 5 h. No peak of reactants was found in the XRD patterns of the produced fluorides. CeO$_2$ and Nd$_2$O$_3$ powders were completely fluorinated by the gas-solid reaction. Figure 5 shows the variation of fractional conversion with time during the fluorination of CeO$_2$ powders with the average diameter of 1.2 µm. It took about 30 min for the complete fluorination of the oxide at 300°C. In the case of CeO$_2$ particle with a diameter of about 3 mm, it took more than 3 h for the complete fluorination of the oxide at 500°C as shown in Figure 6. The fractional conversion increased with an increasing reaction temperature at both particle sizes.

The reaction between Nd$_2$O$_3$ and HF can be represented with the equation (1). As shown in Figure 7, Nd$_2$O$_3$ reacted quickly with HF gas. At 300°C, the fluorination reaction was terminated within 15 min. The fractional conversion of Nd$_2$O$_3$ also increased with the increasing reaction temperature.

From the above results, it was found that rare earth oxides could be fluorinated successfully by the gas-solid reaction. Furthermore, it was concluded that the oxides of transuranic elements could also be fluorinated by the
gas-solid reaction based on the results of CeO$_2$ as a surrogate material for the transuranic oxides.

**Fluorination of SrO, Ag and Pd**

SrO was used for the investigation of the fluorination behavior of alkaline earth elements. Figure 8 shows the result of the fluorination reaction between SrO and HF gas. The fluorination reaction proceeded very quickly. Strontium oxide powders were converted completely to strontium fluoride within 5 min at 300°C.

It is supposed that noble metals are difficult to be fluorinated due to their stability against chemical reaction. It was experimentally verified that the noble metals could not be fluorinated under the conditions of this study. Figure 9 and 10 show the XRD patterns of Ag and Pd powders, respectively, along with their reaction products. No fluorination reaction was preceded after 5 h at 500°C (b) and 700°C (c). Therefore, by using this result, noble metals can be separated from other elements during the dissolution step of the prepared fluorides after fluorination since the densities of noble metals are higher than that of the molten salt. The noble metals separated from the high-level radioactive wastes can be used for the industrial purposes [12,13].

From the above results and the results of Kwon and coworkers [9], it could be concluded that the gas-solid reaction is favorable for the fluorination of the studied metals and oxides except for noble metals.

**Reaction models**

It is important to investigate the reaction model for the reaction kinetic study. Among the various gas-solid reaction models, the most suitable model can be selected by the comparison between the reduced time fractional conversion curve and the experimental values [14]. Some widely used gas-solid reaction models are the diffusion-controlled model, phase boundary model, order of reaction model, and nucleation and growth model as
Table 1. Solid State Reaction Equations. ($\alpha$: fractional conversion, $k$: reaction rate constant, $r$: radius of solid sphere, $u$: constant velocity of interface movement, and $t$: time)

<table>
<thead>
<tr>
<th>Reaction model</th>
<th>Equation</th>
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<tbody>
<tr>
<td>Diffusion controlled reaction (Ginstling-Brounshtein)</td>
<td>$(1-2\alpha/3)(1-\alpha)^{1/3} = (kr^2)\frac{1}{t}$</td>
</tr>
<tr>
<td>Diffusion controlled reaction (Jandar)</td>
<td>$[1-(1-\alpha)^{1/3}]^3 = (kr^2)\frac{1}{t}$</td>
</tr>
<tr>
<td>Phase boundary controlled reaction</td>
<td>$[1-(1-\alpha)^{1/3}]^2 = (ur^2)\frac{1}{t}$</td>
</tr>
<tr>
<td>Order of reaction</td>
<td>$ln(1-\alpha) = -kt$</td>
</tr>
<tr>
<td>Nucleation and growth</td>
<td>$[- ln(1-\alpha)]^{1/2} = kt$</td>
</tr>
</tbody>
</table>

Figure 11. Fractional conversion of CeO$_2$ vs. $t/t_{0.5}$ calculated from various solid state reaction equations.

Figure 11 shows the reduced time-conversion curves for the reaction of CeO$_2$. From the curve, the phase boundary controlled (reaction controlled) model was found to be most suitable for the reaction. The relation between fractional conversion and reaction time is as follows:

$$R(\alpha) = [1 - (1-\alpha)^{1/3}] = (ur)t, \quad (3)$$

where $\alpha$ is fractional conversion, $u$ is constant velocity of interface movement, $r$ is radius of solid sphere, and $t$ is time. It is convenient to use a reduced time ($t/t_{0.5}$) scale for the comparison of experimental results with the equation (3). $t_{0.5}$ is the time at $\alpha = 0.5$. Then

$$R(0.5) = 0.2063 = (ur)t_{0.5} \quad (4)$$

Equation (3) and (4) give

$$R(\alpha) = 0.2063 (tt_{0.5}) \quad (5)$$

Figure 12 and 13 show the reduced time-conversion curve for the reaction of Nd$_2$O$_3$ and SrO, respectively. From the reduced time-conversion curve, the nucleation and growth model was found to be most suitable for the fluorination reaction of both Nd$_2$O$_3$ and SrO. The relation between the fractional conversion and the reaction time

Figure 12. Fractional conversion of Nd$_2$O$_3$ vs. $t/t_{0.5}$ calculated from various solid state reaction equations.

for the model is as follows:

$$A(\alpha) = \sqrt{-\ln(1-\alpha)} = kt = 0.8326t/t_{0.5} \quad (6)$$

where $\alpha$ is fractional conversion, $k$ is reaction rate constant, and $t$ is time.

From the above models, the reaction time for the fluorination of CeO$_2$, Nd$_2$O$_3$, and SrO spheres could be predicted from equation (3) and (6). The predicted time
is useful for the design and the operation of the fluorination reactor.

Even though it was found that the gas-solid reaction method was appropriate for the fluorination of some oxides in the present study, it is still necessary to investigate the various kinds of elements for the development of the fluorination process of metals and metal oxides.

**Conclusions**

The following conclusions can be drawn from this study on the fluorination of metals and metal oxides.

1) CeO$_2$, Nd$_2$O$_3$ and SrO were successfully fluorinated by the reaction with HF gas, and it may be deduced that transuranic oxides could also be fluorinated by the gas-solid reaction method.

2) Fractional conversion of CeO$_2$, Nd$_2$O$_3$ and SrO increased with an increasing reaction temperature.

3) Noble metals did not react with HF gas and they could be separated from other elements during the dissolution step.

4) Among the various gas-solid reaction models, the phase boundary controlled (reaction controlled) model was suitable for the fluorination of CeO$_2$, whereas the nucleation and growth model was suitable for Nd$_2$O$_3$ and SrO.

**Acknowledgement**

This project has been carried out under the Nuclear R&D Program by MOST.

**References**