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Fluorination of niobium compounds with fluorine for fluoride volatility method



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ABSTRACT

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Niobium is one of the fission products contained in spent nuclear fuel. Since niobium pentafluoride (NbF₅) has high volatility, it is considered that niobium volatilizes with uranium hexafluoride when applying the fluoride volatility method, which is a promising pyro-reprocessing method. In this study, fluorination behavior characteristics of niobium compounds, such as reaction temperature, volatility, and reaction path, were investigated by thermogravimetric and differential thermal analyses and X-ray diffraction analysis. The target compounds

acteristics of niobium compounds, such as reaction temperature, volatility, and reaction path, were investigated by thermogravimetric and differential thermal analyses and X-ray diffraction analysis. The target compounds were niobium metal, the niobium oxides NbO, Nb₂O₃, NbO₂ and Nb₂O₅, and niobium oxyfluoride (NbO₂F). All the niobium compounds reacted exothermically and were volatilized completely by the reaction with F_2 . It was considered that niobium volatilized as NbF₅. The fluorination reactions started respectively at 180, 200, 300, and 300 °C for niobium metal, NbO, NbO₂ and Nb₂O₅. In the fluorination of niobium oxides, the intermediate product NbO₂F was also fluorinated above 300 °C and volatilized completely. Nb₂O₃, which seemed to be a mixture of NbO and NbO₂, reacted with F_2 as described by the summation of the fluorination reactions of NbO and NbO₂. The reaction mechanism for the fluorination of niobium compounds obtained in this study is applicable to evaluation of the niobium transfer phenomena in the reprocessing process of the fluoride volatility method.

1. Introduction

The fluoride volatility method is one of the promising pyro-reprocessing methods for spent nuclear fuel that have been developed by several research groups [1-7]. Following the severe accident at the Fukushima Daiichi NPP, this method was investigated as a means for treating the fuel debris produced in the accident [8]. In applying the method, the spent nuclear fuel reacts with a fluorinating agent such as F₂, NF₃, ClF₃, and BrF₅ [9,10]. The elements in the spent fuel are separated into a number of elemental groups depending on the difference in vapor pressure of the fluorinated products. For example, uranium and plutonium are fluorinated respectively to gaseous UF₆ and PuF₆. However, PuF₆ is thermodynamically unstable and gradually decomposes to non-volatile PuF₄ solid [11]. On the other hand, some fission products (FPs) become non-volatile fluorides such as SrF2 and LaF3 and are recovered as solid components and separated from gaseous UF₆. Other FPs form volatile fluorides and are co-volatilized with UF₆ gas. For this reason, separation methods such as distillation and adsorption methods have also been developed for separating FPs from UF_6 [1–7]. From this viewpoint, the transfer mechanism of FPs should be clarified to design the process of the fluoride volatility method. Therefore, it is important to understand the fluorination behaviors of FPs. The authors previously investigated the fluorination behavior of antimony compounds [12]. In the work reported in this paper, we studied the fluorination behavior of niobium, another of the volatile FP fluorides. Incidentally, the fluorinated FPs can be converted to oxide forms by using a steam oxidation method [6,7] and finally disposed of as vitrified waste.

Niobium is one of the FPs contained in spent nuclear fuel. One reported amount of niobium in the spent fuel is 5 mg/tHM [13], which is smaller than that of other FPs. However, niobium has radioactivity and forms volatile fluorides such as NbF₅ for which vapor pressure is 100 kPa at 234 °C [1]. Therefore, niobium may volatilize in the fluoride volatility method if NbF₅ is formed by the fluorination reaction. For this reason, niobium is considered an important element for the fluoride volatility method. Kleykamp [14] reported that niobium was contained as oxides in spent nuclear fuel. Since the fluoride volatility method may also be applicable to metal fuel, it has been considered desirable to clarify the fluorination reactions for niobium metal and oxides.

Experimental investigations have already been carried out on the fluorination reactions of niobium compounds [15–17]. Junkins et al. [15] reported that NbF_5 was obtained by fluorinating niobium metal

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with F_2 in a nickel reactor at 300 °C. Rakov et al. [16] determined the reaction rates of the fluorination reactions of Nb₂O₅ and NbO₂F within the range from 330 to 430 °C. However, it has been considered necessary to further investigate fluorination behavior characteristics such as reaction temperature and reaction path. Additionally, to the best of the authors' knowledge, no reports have been published about the fluorination reactions of the other niobium oxides NbO, Nb₂O₃, and NbO₂. These reactions should be investigated to facilitate understanding of the fluorination behavior of niobium compounds with F_2 .

In this research we experimentally investigated fluorination behavior characteristics such as reaction temperature, volatility and reaction path for several niobium compounds. The target compounds for fluorination were niobium metal, the niobium oxides NbO, Nb₂O₃, NbO₂ and Nb₂O₅, and niobium oxyfluoride (NbO₂F). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) using a thermogravimeterdifferential thermal analyzer and X-ray diffraction (XRD) analysis were used in the investigation.

2. Results and discussion

Fluorination experiment results are shown in Section 2.1 for each niobium compound. The results of thermodynamic consideration on related reactions are given in Section 2.2. Finally, on the basis of these results, fluorination behavior is discussed in Section 2.3 for each niobium compound.

2.1. Results of fluorination of niobium compounds with fluorine

2.1.1. Niobium metal

The TG-DTA curve of the reaction of niobium metal with F_2 is shown in Fig. 1. The temperature was increased from room temperature to 400 °C at a 10 °C/min heating rate. The mass change ratio (Δ M) of a sample obtained by TG is shown as solid lines in the figure. The heat transfer obtained by DTA is shown as dashed lines; an upward signal means the reaction was exothermic.

As shown in the figure, the ΔM started to decrease with the exothermic reaction above 180 °C. This indicates that niobium metal reacted exothermically with F₂ above 180 °C. The ΔM reached about -100% at the end of the reaction, showing that niobium metal was completely volatilized by the fluorination with F₂. Since the ΔM decreased simply with an exothermic peak, the fluorination of niobium metal seemed to proceed by a single-step reaction.

To investigate the reaction path, we carried out XRD analysis of the residue of the fluorination reaction. The residue was prepared by an additional fluorination experiment. The F_2 flow was stopped at around 210 °C during the experiment, the heating rate for which was 10 °C/min. Only a niobium metal phase was identified in the diffraction pattern of the residue and no peaks of any other niobium products were observed. This suggests that niobium metal was directly fluorinated to a



Fig. 1. TG-DTA curves of the niobium metal fluorination experiment with F_2 at a 10 $^\circ C/min$ heating rate.



Fig. 2. TG-DTA curves of the Nb_2O_5 fluorination experiment with F_2 at three heating rates: (a) 10 °C/min, (b) 5 °C/min, and (c) 2 °C/min.

volatile product by the reaction with F₂.

2.1.2. Nb₂O₅

The TG-DTA curve of the reaction of Nb₂O₅ with F_2 is shown in Fig. 2. The temperature was increased from room temperature to 500 °C. The heating rates for (a), (b), and (c) were respectively 10, 5, and 2 °C/min. In (c), the temperature was increased from room temperature to 250 °C at a 10 °C/min heating rate to shorten the experiment time. Since the heating rate was changed during the experiment, the baseline of the DTA curve in (c) changed at 250 °C unintentionally.

As shown in Fig. 2, the Δ M started to decrease with the exothermic reaction above 300 °C and reached about -100% at the end of the experiment. This indicates that Nb₂O₅ reacted with F₂ exothermically and the sample was volatilized completely. At a slower heating rate, the F₂ feed time per unit temperature increase became longer. For this reason, the temperature at which niobium was completely volatilized shifted to lower one for a slower heating rate; actually, the volatilization of niobium was completed respectively at 490, 430, and 400 °C for (a), (b), and (c). When the heating rate was faster than the reaction rate, the temperature increased before the reaction was finished. Therefore, the heating rate affected the shift of the TG-DTA curve. Actually, the peak temperature of the first exothermic reaction shifted to a higher temperature as the heating rate increased. However, the difference in the heating rate did not seem to affect the reaction mechanism because the TG-DTA curves in (a), (b), and (c) resembled each other.

In (a)–(c), two exothermic peaks were observed above 300 °C and the trend of decreasing ΔM also seemed to change with the first peak. This indicates that a two-step reaction occurred in the fluorination of Nb₂O₅.

To investigate the reaction path, we identified the intermediate product of the fluorination reaction by XRD analysis. The TG-DTA curve of the fluorination experiment for preparing the intermediate product is shown in Fig. 3. In this experiment the heating rate was 10 °C/min, the amount of Nb₂O₅ (about 10 mg) was larger than the standard experimental condition indicated in Section 4, and the flow rate of 10% F_2 -N₂



Fig. 3. TG-DTA curves of the Nb_2O_5 fluorination experiment with F_2 at a 10 $^\circ\text{C}/$ min heating rate.

gas (10 mL/min) was half of the condition. For this reason, 85 mass % of the starting Nb₂O₅ remained in the pan after the experiment. Since one exothermic peak followed by another appeared at 450 °C in Fig. 3, we considered the residue to be the product of the first exothermic reaction of the two found in Fig. 2. XRD analysis identified this product as NbO₂F and no peaks corresponding to other phases such as Nb₂O₅ and other oxyfluorides were observed in the XRD pattern. This indicates that Nb₂O₅ was completely converted to NbO₂F by the first exothermic reaction and after that all the niobium was volatilized by the second reaction.

2.1.3. NbO₂F

To further investigate the fluorination reaction of Nb₂O₅, we carried out a fluorination experiment for NbO₂F, which was the intermediate fluorination product of Nb₂O₅. The TG-DTA curve of the reaction of NbO₂F with F_2 at a 5 °C/min heating rate is shown in Fig. 4. The NbO₂F powder was prepared by the experiment mentioned in Section 2.1.2.

Above 300 °C, the ΔM started to decrease with an exothermic peak. At the end of the experiment NbO₂F was completely volatilized. Since only one exothermic peak was observed (Fig. 4) and the ΔM simply decreased, it can be considered that NbO₂F reacted with F₂ in a singlestep reaction.

2.1.4. NbO₂

Next, we carried out a fluorination experiment for NbO₂, which has a lower niobium valency than Nb₂O₅ and NbO₂F have. The TG-DTA curve of the reaction of NbO₂ with F₂ is shown in Fig. 5. The heating rate was 5 °C/min. A sharp exothermic peak was observed at 300 °C and the mass of the sample slightly increased by about 1%. A decrease in the Δ M with two exothermic peaks followed and the entire sample was volatilized at the end of the experiment.

To investigate the reaction path, we identified the intermediate products of the fluorination reactions by XRD analysis. The products



Fig. 4. TG-DTA curves of the NbO_2F fluorination experiment with F_2 at a 5 $^\circ\text{C}/$ min heating rate.



Fig. 5. TG-DTA curves of the $\rm NbO_2$ fluorination experiment with $\rm F_2$ at a 5 $^\circ C/$ min heating rate.

were prepared by two additional fluorination experiments. In the first, the temperature was increased from room temperature to 310 °C at a 10 °C/min heating rate and then kept at 310 °C for 5 min. In the second, the temperature was increased from room temperature to 360 °C at a 10 °C/min heating rate and then kept at 360 °C for 20 min. The XRD patterns of the products prepared by the first and second experiments are shown respectively in Fig. 6(a) and (b). As shown in (a), the product obtained by the fluorination reaction at 310 °C was identified as mainly NbO₂ and contained a small amount of NbO₂F. No peaks corresponding to other phases such as those for other oxyfluorides were observed in the XRD pattern. On the other hand, as shown in (b), the product obtained by the fluorination reaction at 360 °C was identified as NbO₂F. Since a polyimide tape was used to avoid air-oxidation of the sample during the XRD measurement, broad peaks due to the tape material appeared in the 20 range from 20 to 28 degrees. For comparison, the XRD pattern of the polyimide tape is shown in (c). These results indicated that a part of the NbO2 was fluorinated to NbO2F by the first exothermic reaction at 300 °C, complete fluorination to NbO₂F followed in the second, and all the niobium was volatilized by the third.

2.1.5. NbO

We next investigated the fluorination reaction for NbO, which has the lowest niobium valency among the studied niobium oxides. The TG-DTA curve of the reaction of NbO with F₂ is shown in Fig. 7. The heating rate was 5 °C/min. The ΔM started to decrease with the continuous exothermic peak above 200 °C. Some exothermic reactions were observed and the decrease in the ΔM changed step by step, indicating some species might form in the fluorination reaction of NbO. All of the NbO was volatilized at the end of the experiment.

To investigate the reaction path, we identified the intermediate products of the fluorination reactions by XRD analysis. The products



Fig. 6. XRD patterns of the residue for the NbO₂ fluorination experiment. (a) product after fluorination at 310 °C, (b) product after fluorination at 360 °C, and (c) only polyimide tape for comparison.



Fig. 7. TG-DTA curves of the NbO fluorination experiment with $\rm F_2$ at a 5 $^{\circ}\rm C/min$ heating rate.



Fig. 8. XRD patterns of the residue for the NbO fluorination experiment. (a) product after fluorination at 240 $^\circ C$ and (b) product after fluorination at 310 $^\circ C$.

were prepared by two additional fluorination experiments. In the first, the temperature was increased from room temperature to 240 °C at a 10°C/min heating rate and then kept at 240°C for 30 min. In the second, the temperature was increased from room temperature to 310 °C at a 10 °C/min heating rate and then kept at 310 °C for 40 min. The XRD patterns of the products prepared by the first and second experiments are shown respectively in Fig. 8(a) and (b). As shown in (a), the product obtained by the fluorination reaction at 240 °C was identified as mainly NbO and contained a small amount of NbO₂F. No peaks corresponding to other phases such as other oxyfluorides were observed in the XRD patterns. On the other hand, as shown in (b), the product obtained by the fluorination reaction at 310 °C was identified as NbO₂F. Since the polyimide tape was used only for the XRD analysis of (a), broad peaks for it appeared in the 20 range from 20 to 28 degrees. These results indicated that a part of NbO was fluorinated to NbO₂F with the first exothermic reaction at 200 °C followed by complete fluorination to NbO₂F in the second reaction. After that, all the niobium was volatilized by the third reaction.

2.1.6. Nb₂O₃

Finally, the TG-DTA curve of the reaction of Nb₂O₃ with F₂ is shown in Fig. 9. The heating rate was 10 °C/min. The exothermic reaction started above 200 °C and four exothermic peaks were found at 230, 300, 350, and 440 °C (Fig. 9). The Δ M started to decrease above about 230 °C and the Δ M curve changed with the peaks. Finally, the entire sample was volatilized at the end of the experiment. Nb₂O₃ of 99.9% purity (Kojundo Chemical Laboratory Co., Ltd.) was used as received. The XRD pattern of the Nb₂O₃ used in this study is shown in Fig. 10. Peaks for NbO and NbO₂ phases were observed in the pattern, suggesting the Nb₂O₃ we used was a mixture of NbO and NbO₂.

2.2. Thermodynamic consideration of fluorination of niobium compounds

This section describes the thermodynamic consideration results of the fluorination reaction of niobium compounds. We evaluated the



Fig. 9. TG-DTA curves of the Nb_2O_3 fluorination experiment with F_2 at a 10 $^\circ\text{C}/$ min heating rate.

Gibbs free energies (Δ G) for the related fluorination reactions by calculation using a thermodynamic database [18] and the results are shown in Fig. 11. Since data for NbO₂F are missing, the related reactions for it are not given in the figure.

In the temperature range from room temperature to 500 °C, the ΔG of the fluorination reactions of the niobium compounds were negative. Therefore, it can be considered that NbF₅ was formed by the reactions at this temperature range. On the other hand, the ΔG of the reactions took large negative values in the order of niobium metal, NbO, NbO₂, and Nb₂O₅. This order seemed to relate to the order of the valence state of niobium. For example, the change in the valence state was largest for the fluorination of niobium metal; the state changed from zero to pentavalent. Together with the ΔG calculation results, this seemed to indicate that the niobium compounds with lower valence state were more reactive for the fluorination reaction. This suggests that the oxidation reaction from lower valence state to higher one occurs first followed by the exchange reaction of oxygen by F₂.

2.3. Fluorination reaction of niobium compounds

2.3.1. Niobium metal

As mentioned in Section 2.1.1, niobium metal was directly fluorinated to a volatile product by a single-step reaction. The thermodynamic consideration shown in Fig. 11 leads to the evaluation that NbF₅ was produced by the fluorination reaction of niobium metal. Junkins et al. [15] reported that NbF₅ was formed by the reaction of niobium metal with F₂ at 300 °C. On the basis of this report and our obtained results, we considered the following reaction (1) is the fluorination reaction of niobium metal.

$$2/5Nb + F_2 \rightarrow 2/5NbF_5 \tag{1}$$

We also confirmed that this reaction started above 180 °C.

2.3.2. Nb₂O₅ and NbO₂F

As mentioned in Section 2.1.2, Nb₂O₅ was fluorinated by a two-step reaction above 300 °C; NbO₂F was generated in the first step and all the niobium was volatilized in the second. Additionally, as mentioned in Section 2.1.3, NbO₂F was fluorinated to a volatile product by a singlestep reaction above 300 °C because Δ M simply decreased with an exothermic peak (Fig. 4). NbF₅ and NbOF₃ were possible volatile products of the fluorination reaction of NbO₂F. However, Rakov et al. [16] suggested that NbF₅ was formed by the fluorination of NbO₂F. Therefore, we consider that NbOF₃ was not formed in the fluorination reaction and that even if it had been it would have immediately been fluorinated to NbF₅.We therefore consider that the following reactions (2) and (3) describe the fluorination of Nb₂O₅.

$$Nb_2O_5 + F_2 \rightarrow 2NbO_2F + 1/2O_2$$
 (2)

$$1/2NbO_2F + F_2 \rightarrow 1/2NbF_5 + 1/2O_2$$
 (3)



Fig. 10. XRD pattern of the Nb₂O₃ used in this study.



Fig. 11. Gibbs free energies of the fluorination reactions of niobium compounds.

The calculated ΔM value for the fluorination from Nb₂O₅ to NbO₂F was + 8%. However, in Fig. 2, the decrease in ΔM seemed to stop temporally at the first exothermic reaction, although the value of ΔM did not increase over + 8%. This is due to the formation of NbO₂F and the subsequent formation of volatile NbF₅.

In this research, we clarified experimentally that these two reactions started above 300 °C at the same time, that NbO₂F was formed in the first reaction. And it was considered that NbO₂F was volatilized by the further fluorination to NbF₅ in the second reaction.

2.3.3. NbO₂

As mentioned in Section 2.1.4, NbO₂ was fluorinated by three stepexothermic reactions above 300 °CA part of the NbO₂ was fluorinated to NbO₂F in the first step, complete fluorination to NbO₂F followed in the second, and all of the niobium was volatilized in the third. These results indicate the first and second exothermic reactions are as follows.

$$2NbO_2 + F_2 \rightarrow 2NbO_2F \tag{4}$$

Piennar et al. [17] have reported that NbO₂F was decomposed above 655 °C. This means that NbO₂F remains a solid component at 300 °C. The calculated ΔM value for the fluorination from NbO₂ to NbO₂F is + 15%. Since the increase in the ΔM was only 1% at 300 °C and the residue was mainly NbO₂, the fluorination reaction at 300 °C seemed to be a surface reaction. If NbO₂F were near the surface it might prevent the F₂ from coming into contact with NbO₂ in bulk and stop the fluorination reaction on the surface. On the other hand, NbO₂ was completely converted to NbO₂F at 360 °C as shown in Fig. 6(b). This means that reaction (4) proceeded in bulk in the second exothermic reaction shown in Fig. 5. The third exothermic reaction, for which the peak temperature was 430 °C (Fig. 5), corresponds to the fluorination reaction of NbO₂F and that reaction is described as reaction (3).

The fluorination reaction of NbO₂ showed a sharp exothermic peak at 300 °C that was not found in the fluorination reaction of Nb₂O₅. The valence state of niobium of NbO₂ is smaller than that of Nb₂O₅. As

mentioned in Section 2.2, the ΔG of the fluorination reaction shown in Fig. 11 seems to indicate that niobium compounds having a lower niobium valence state are more reactive for the fluorination reaction. For this reason, a sharp exothermic peak for the reaction was observed at 300 °C, which is a lower peak temperature than the 380 °C of the Nb₂O₅ fluorination reaction.

2.3.4. NbO

As mentioned in Section 2.1.5, NbO reacted with F_2 above 200 °C and NbO₂F was formed from the reaction. Since ΔM started to decrease at 200 °C (Fig. 7), a volatile product was also formed concurrently above 200 °C. It was necessary to add oxygen to form NbO₂F from the fluorination of NbO. However, since oxygen gas was not contained in the feed gas in the experiment, it appears that the following reaction (5) occurred.

$$2/3NbO + F_2 \rightarrow 1/3NbF_5 + 1/3NbO_2F$$
 (5)

In this reaction, volatile NbF₅ was formed and the Δ M actually started to decrease above 200 °C (Fig. 7). Then, NbO₂F was formed using oxygen generated by the NbF₅ generation reaction from NbO. On the other hand, NbO was completely converted to NbO₂F at 310 °C as shown in Fig. 8(b). When reaction (5) was completed, the Δ M was -34%. Actually, around about 330 °C, at which the Δ M reached -34%, the exothermic reaction came to an end and the decreasing trend of the Δ M changed (Fig. 7). This led us to believe that the fluorination reaction observed from 200 to 330 °C in Fig. 7 was reaction (5). On the other hand, the last exothermic peak at 400 °C (Fig. 7) corresponded to the fluorination reaction of NbO₂F and was described as reaction (3).

The starting temperature of the fluorination reaction for NbO (200 °C) was lower than that for NbO₂ (300 °C) and Nb₂O₅ (about 330 °C). As mentioned in Section 2.2, niobium compounds with lower valence state seemed to be more reactive for the fluorination reaction. Actually, the starting temperature of the fluorination reaction for NbO₂ was lower than that for Nb₂O₅ as mentioned in Section 2.3.3. For this reason, we felt that the starting temperature of the fluorination reaction for NbO would be the lowest (e.g., 200 °C) among the niobium oxides.

The fluorination reaction of NbO₂ started at 300 °C, but stopped during the course of the reaction. It can be considered that the reason for this is that solid NbO₂F covering the surface prevented the fluorination reaction. On the other hand, NbO was fluorinated in bulk even at 300 °C. The fluorination reaction of NbO can be completed in bulk at such a low temperature because, as shown in reaction (5), NbO₂F and volatile NbF₅ are concurrently generated in the fluorination reaction of NbO.

2.3.5. Nb₂O₃

Finally, we will briefly discuss the fluorination reaction of Nb_2O_3 because the Nb_2O_3 used in this experiment was identified as a mixture of NbO and NbO₂ on the basis of XRD analysis. As mentioned in Section 2.1.6, four exothermic peaks were found at 230, 300, 350, and 440 °C (Fig. 9). The peaks at 230 and 300 °C seemed to be similar to those found in the fluorination reaction of NbO (Fig. 7), while those at 350 and 440 °C (Fig. 5). Therefore, we believe that the fluorination reaction of NbO₂ (Fig. 5). Therefore, as the summation of the fluorination reactions of NbO and NbO₂.

3. Conclusion

To ascertain the fluorination behavior of niobium in spent nuclear fuel in the fluoride volatility method, we investigated the reactions of niobium metal and the niobium oxides NbO, Nb₂O₃, NbO₂, and Nb₂O₅ with F_2 by TG-DTA and XRD analyses. We found that niobium metal exothermically reacted with F_2 and was volatilized completely above 200 °C, and consider that NbF₅ was directly formed by the reaction.

NbO₂ and Nb₂O₅ exothermically reacted with F₂ above 300 °C and NbO₂F was formed as the intermediate product of the fluorination reactions. NbO₂F also exothermically reacted with F₂ and was volatilized completely above 300 °C; it can be considered that volatile NbF₅ was formed by the fluorination reaction. NbO exothermically reacted with F₂ above 200 °C and formation of NbO₂F and volatilization of niobium occurred concurrently; niobium was volatilized as NbF₅ in this reaction. Nb₂O₃, which was identified as a mixture of NbO and NbO₂, reacted with F₂ as described by the summation of the fluorination reactions of NbO and NbO₂.

4. Experimental

4.1. Materials

Niobium metal of 99.5% purity and Nb₂O₅ of 99.9% purity (all from Wako Pure Chemical Industries, Ltd.) and Nb₂O₃ of 99.9% purity (Kojundo Chemical Laboratory Co., Ltd.) were used as received. NbO (purity was not provided) and NbO₂ of 99.9% purity (all from Kojundo Chemical Laboratory Co., Ltd.) were used after they were ground with a mortar. All of the niobium compounds were fine powder form. Analytical grade 10% F_2 -N₂ (90.1% N₂ and 9.9% F_2) (Central Glass Co., Ltd.) were used as received.

4.2. Thermogravimetric and differential thermal analyses

For these analyses we used the Rigaku TG-DTA system (Thermo plus 2) set in a high purity argon atmosphere glove box. To prevent corrosion by F_2 , nickel or nickel alloy was used in the TG-DTA system and in the pan for the TG-DTA. The amount of sample for an experimental run was about 3 mg. The flow gas was a mixture of Ar (40 mL/min) and 10% F_2 -N₂ (20 mL/min). F_2 in off-gas was eliminated by an adsorption method using Al₂O₃ adsorbent. Heating was carried out from room temperature to 500 °C at heating rates of 2, 5, and 10 °C/min.

4.3. X-ray diffraction analysis

We identified the residue of the fluorination experiment by X-ray powder diffraction with the Rigaku Type MiniFlex600 diffractometer with Ni filtered Cu K α irradiation (15 kV and 40 mA) equipped with a D/tex Ultra detector. The sample on the glass holder for XRD analysis was covered as necessary using polyimide film to prevent exposure to air. The phases observed in the diffraction pattern were analyzed by the PDXL2 program using the ICDD powder diffraction file.

References

- A.A. Jonke, Reprocessing of nuclear reactor fuel by processes based on volatilization, fractional distillation, and selective adsorption, Atomic Energy Rev. 3 (1965) 3–60.
- [2] V.V. Shatalov, M.B. Seregin, V.F. Kharin, L.A. Ponomarev, Gas-fluoride technology for processing spent oxide fuel, Atomic Energy 90 (2001) 224–234.
- [3] J. Uhlíř, M. Mareček, Fluoride volatility method for reprocessing of LWR and FR fuels, J. Fluorine Chem. 130 (2009) 89–93.
- [4] G. Vandenbussche, Étude cinétique de la fluoration par le fluor de quelques composés de l'uranum et du plutonium, CEA-R2859 (1965).
- [5] M. Iwasaki, Kinetics of the fluorination of uranium dioxide pellets by fluorine, J. Nucl. Mater. 25 (1968) 216–226.
- [6] Y. Kani, A. Sasahira, K. Hoshino, F. Kawamura, New reprocessing system for spent nuclear reactor fuel using fluoride volatility method, J. Fluorine Chem. 130 (2009) 74–82.
- [7] K. Hoshino, D. Watanabe, A. Sasahira, M. Nagata, T. Chikazawa, Y. Sano, F. Kawamura, Development of Advance Reprocessing System "FLUOREX", GLOBAL 2011, Makuhari Japan, 2011.
- [8] T. Fukasawa, A. Sasahira, K. Hoshino, T. Kikuchi, M. Nagata, A. Kirishima, N. Sato, Development of Fuel Debris Treatment Technology by the Fluorination Method, GLOBAL 2015, Paris France, 2015.
- [9] O. Amano, F. Kawamura, T. Fukasawa, M. Takahashi, A. Sasahira, Y. Shibata, J. Yamashita, New Reprocessing Technology, FLUOREX, for LWR Fuel Cycle, GLOBAL 2001, Paris France, 2001.
- [10] B. McNamara, R. Scheele, A. Kozelisky, M. Edwards, Thermal reactions of uranium metal, UO₂, U₃O₈, UF₄, and UO₂F₂ with NF₃ to produce UF₆, J. Nucl. Mater. 394 (2009) 166–173.
- [11] O. Amano, F. Kawamura, M. Aoi, K. Hoshino, A. Sasahira, Y. Kani, V.N. Prusakov, Verification of Key Technologies for FLUOREX, the New Reprocessing System LWR Fuel Cycle, GLOBAL 2003, New Orleans USA, 2003.
- [12] D. Watanabe, D. Akiyama, N. Sato, Reactions of antimony compounds with fluorine gas by thermogravimetric and differential thermal analyses and X-ray diffraction analysis, J. Fluorine Chem. 214 (2018) 1–7.
- [13] S. Honma, Handbook on Process and Chemistry of Nuclear Fuel Reprocessing 3rd Edition, JAEA-Review 2015-002, 2015 [in Japanese].
- [14] H. Kleykamp, The chemical state of the fission products in oxide fuels, J. Nucl. Mater. 131 (1985) 221–246.
- [15] J.H. Junkins, R.L. Farrar Jr., E.J. Barber, H.A. Bernhardt, Preparation and Physical Properties of Niobium Pentafluoride, Fluorine Chemistry Symposium, New York, 1951.
- [16] É.G. Rakov, D.S. Kopchikhin, B.N. Sudarikov, B.V. Gromov, Fluorination kinetics of Nb₂O₅, Soviet Atomic Energy 31 (1971) 137.
- [17] A.D. Pienaar, J.B. Wagener, P.L. Crouse, Niobium and tantalum separation by gasphase fluorination, Int. J. Miner. Process. 114-117 (2012) 7–10.
- [18] Thermodynamic database MALT group, Thermodynamic Database MALT for Windows, Kagaku Gijutsu-Sha, Tokyo, 2005 [CD-ROM].