Fluorination of niobium compounds with fluorine for fluoride volatility method

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ABSTRACT

Niobium is one of the fission products contained in spent nuclear fuel. Since niobium pentafluoride (NbF_5) 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 were niobium metal, the niobium oxides NbO, Nb_2O_3, NbO_2 and Nb_2O_5, and niobium oxyfluoride (NbO_2F). All the niobium compounds reacted exothermically and were volatilized completely by the reaction with F_2. It was considered that niobium volatilized as NbF_5. The fluorination reactions started respectively at 180, 200, 300, and 300 °C for niobium metal, NbO, NbO_2 and Nb_2O_5. In the fluorination of niobium oxides, the intermediate product NbO_2F was also fluorinated above 300 °C and volatilized completely. Nb_2O_3, which seemed to be a mixture of NbO and NbO_2, reacted with F_2 as described by the summation of the fluorination reactions of NbO and NbO_2. 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 F_2, NF_3, ClF_3, and BrF_5 [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 UF_6 and PuF_6. However, PuF_6 is thermodynamically unstable and gradually decomposes to non-volatile PuF_4 solid [11]. On the other hand, some fission products (FPs) become non-volatile fluorides such as SrF_2 and LaF_3 and are recovered as solid components and separated from gaseous UF_6. Other FPs form volatile fluorides and are co-volatilized with UF_6 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 NbF_5 for which vapor pressure is 100 kPa at 234 °C [1]. Therefore, niobium may volatilize in the fluoride volatility method if NbF_5 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 Nb_2O_5 and NbO_2F 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, Nb_2O_3, and NbO_2. 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, Nb_2O_3, NbO_2 and Nb_2O_5, and niobium oxyfluoride (NbO_2F). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) using a thermogravimeter-differential 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 (ΔM) 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 F_2 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 F_2. 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
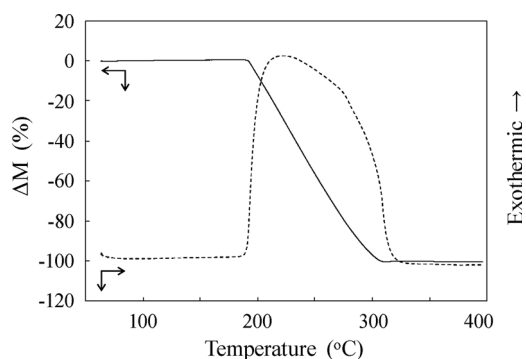

Fig. 1. TG-DTA curves of the niobium metal fluorination experiment with F_2 at a 10 °C/min heating rate.
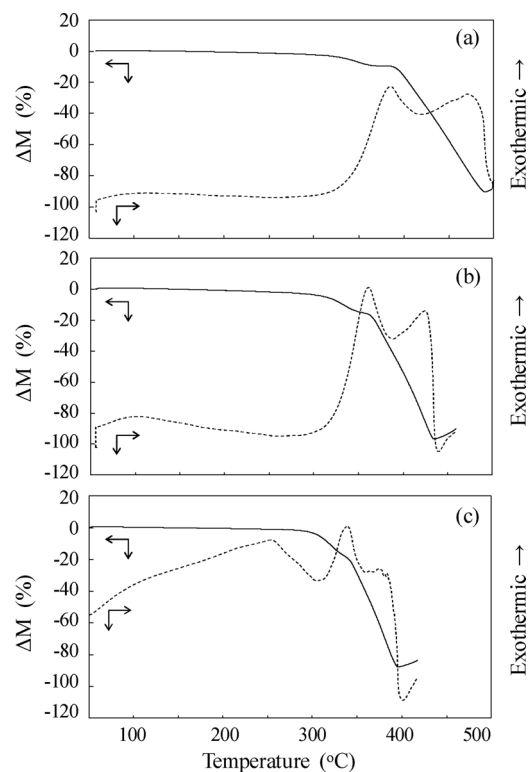

Fig. 2. TG-DTA curves of the Nb_2O_5 fluorination experiment with F_2 at three heating rates: (a) 10 °C/min, (b) 5 °C/min, and (c) 2 °C/min.

volatile product by the reaction with F_2.

2.1.2. Nb_2O_5

The TG-DTA curve of the reaction of Nb_2O_5 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 ΔM started to decrease with the exothermic reaction above 300 °C and reached about -100% at the end of the experiment. This indicates that Nb_2O_5 reacted with F_2 exothermically and the sample was volatilized completely. At a slower heating rate, the F_2 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 Nb_2O_5.

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 Nb_2O_5 (about 10 mg) was larger than the standard experimental condition indicated in Section 4, and the flow rate of 10% F_2-N_2