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Reactions of antimony compounds with fluorine gas by thermogravimetric and differential thermal analyses and X-ray diffraction analysis

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ABSTRACT

Antimony is one of the key fission products in the reprocessing of spent nuclear fuel by the fluoride volatility method because of the high volatility of antimony fluorides. Since the fluorination reaction of antimony compounds is not well understood, the reaction behavior of antimony compounds with F_2 was investigated by thermogravimetric and differential thermal analyses and X-ray diffraction analysis in this study. The target antimony compounds were antimony metal, SbF_3, Sb_2O_3, Sb_2O_4, and Sb_2O_5. The fluorination reaction of antimony metal started at 150 °C, and the fluorination product was SbF_3. SbF_3 volatilized completely by the reaction with F_2 above 190 °C; it was considered that volatile SbF_5 was formed by the reaction with F_2. In the series of fluorination of the antimony oxides, Sb_2O_3, Sb_2O_4, and Sb_2O_5, they started to react with F_2 and volatilize at 330 °C as SbF_5. During the fluorination of Sb_2O_3, Sb_2O_4 was formed temporarily in the course of the reaction. Oxygen released from the fluorination reaction of a part of Sb_2O_3 would oxidize remained Sb_2O_3 to Sb_2O_4. The reaction mechanism for the fluorination of antimony compounds obtained in this study is applicable to evaluate the transfer of antimony in the reprocessing process of the fluoride volatility method.

1. Introduction

The fluoride volatility method is one of the promising reprocessing methods of spent nuclear fuel. It was developed by several research groups [1–7], and recently its application to the fuel debris produced by the severe reactor accident has been investigated after the Fukushima Daiichi NPP accident [8]. In the fluoride volatility method, the spent nuclear fuel is reacted with fluorinating agent such as F_2, NF_3, ClF_3, and BrF_5 [9,10]. The elements in the spent nuclear fuel are separated into several elemental groups depending on the difference in vapor pressure of the fluorinated products. For example, uranium and plutonium is fluorinated to UF_6 and PuF_6 gases; however, PuF_6 is thermodynamically unstable and gradually decompose to PuF_4 solid [11]. On the other hand, fluorinated fission products (FPs) such as SrF_2 and LaF_3 have low vapor pressure, therefore, these are recovered as solid components and separated from UF_6 gas. Although, some FPs forms volatile fluorides and co-volatilized with UF_6 gas. For this reason, some separation methods such as a distillation method and an adsorption method are also developed for the separation of FPs from UF_6 gas [1–7]. In order to design the process of the fluoride volatility method, the transfer of FPs should be clarified. Therefore, it is important to understand the fluorination behaviors of FPs. Incidentally, the fluorinated FPs can be converted to oxide forms by a steam oxidation method [6,7], and finally disposed as vitrified waste.

Antimony is one of the FPs contained in spent nuclear fuel. A reported amount of antimony in the spent fuel is 13.6 g/tHM [12]. Antimony forms volatile fluorides such as SbF_5 which vapor pressure is 100 kPa at 142.7 °C [1]. Therefore, antimony may volatilize in the fluoride volatility method if SbF_5 is formed by the fluorination reaction. Because of this reason, antimony is considered as an important element for the fluoride volatility method. Kleykamp [13] reported that antimony was contained as metallic precipitate in spent nuclear fuel. However, in the case of spent high burn-up nuclear fuel, antimony metal may be oxidized to oxide form because of high oxygen potential in the spent nuclear fuel. Therefore, it was considered that fluorination reaction should be clarified for antimony metal and oxides.

Colbin [14] summarized information about some species of antimony compounds and fluorination reactions. It is reported that antimony metal is fluorinated to SbF_3 and SbF_5 by the reaction with F_2, and Sb_2O_3 is fluorinated to SbF_5 by the reaction with the mixed gas of F_2 and N_2 (4:1). However, the reaction temperatures of these reactions were not reported. On the other hand, Komura et al. [15] reported that UO_2 was fluorinated by F_2 to UF_6 via UO_2F_2. This fluorination reaction was considered as an example of fluorination reaction of oxide material.

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Based on this example, oxyfluoride may formed as intermediate product in the fluorination reaction of oxide material. Colbin [14] suggested antimony oxyfluorides such as SbOF, SbO_2F, and $SbOF_3$. Therefore, the fluorination reaction of antimony oxides should be investigated taking into account oxyfluoride formation. However, to the best of the authors' knowledge no reports have been published about the reaction path. Therefore, the reaction temperature and the reaction path of the fluorination reaction of antimony compounds should be evaluated for understanding the behavior of antimony in the fluoride volatility method.

In this research, the reaction temperature and the reaction path of the fluorination reaction were experimentally studied for some species of antimony compounds. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) using a thermogravimeter-differential thermal analyzer and X-ray diffraction analysis (XRD) were carried out. Oxide and metal forms are applied for nuclear fuel; therefore, antimony metal and the antimony oxides, Sb_2O_3, Sb_2O_4, and Sb_2O_5, were used as target compounds for fluorination. Additionally, in order to well understand the fluorination reaction of the antimony compounds, fluorination of SbF_3, a fluorination intermediate, was also investigated.

2. Results and discussion

Results of fluorination experiment are shown in Section 2.1 for each antimony compounds. Next, results of thermodynamic consideration on related reaction are shown in Section 2.2. Finally, based on the results shown in Sections 2.1 and 2.2, fluorination reaction was discussed in Section 2.3 for each antimony compounds.

2.1. Results of fluorination experiment of antimony compounds

2.1.1. Results of fluorination experiment of antimony metal

The TG-DTA curves of the fluorination experiment of antimony metal are shown in Fig. 1. The temperature was heated from room temperature to 500 °C. The heating rates for Fig. 1(a)–(c) were 10, 5, and 2 °C/min, respectively. In order to investigate the effect of heating rate on fluorination reaction, the fluorination experiment was carried out at three heating rates. The mass change (ΔM) of antimony compound obtained by TG is shown as solid lines in Fig. 1. The heat transfer obtained by DTA is shown as dashed lines; upper signal corresponds to the exothermic reaction. The sharp exothermic rising below 100 °C is attributed to the surface fluorination of sample pan made of nickel alloy.

A slight weight increase around 200 °C was observed followed by the rapid weight decrease with several exothermic peaks in Fig. 1(a). This indicates that antimony metal reacted with F_2 exothermically, and antimony metal was temporarily converted to heavier compounds by reaction with F_2 around 200 °C, and finally volatilized by further fluorination. All of the antimony metal was volatilized in Fig. 1(b) and (c), but about 40% of the solid material remained in Fig. 1(a). At slower heating rate, the F_2 feed time per unit temperature increase became longer. Since the F_2 feed time after start of fluorination reaction was enough in the experiment at heating rate of 5 and 2 °C/min, all of the antimony metal was volatilized in Fig. 1(b) and (c). On the other hand, a continuous exothermic peak was observed in Fig. 1(a) and (b), but two exothermic peaks clearly separated with each other were observed in Fig. (c). When the heating rate was fast compered to reaction rate, temperature increased before the reaction was finished. Therefore, heating rate affected shift of TG-DTA curve and peak separation, and heating rates of 10 and 5 °C/min would be too fast to observe two exothermic peaks separately. These two exothermic peaks indicated that the fluorination reaction of antimony metal proceeded by at least two steps; based on Fig. 1(c), these were exothermic reaction with mass increase at 150 °C and exothermic reaction with mass decrease at 190 °C. Additionally, ΔM decreased by about 10% around 330 °C in Fig. (c), therefore, the other reaction was considered to be occurred.

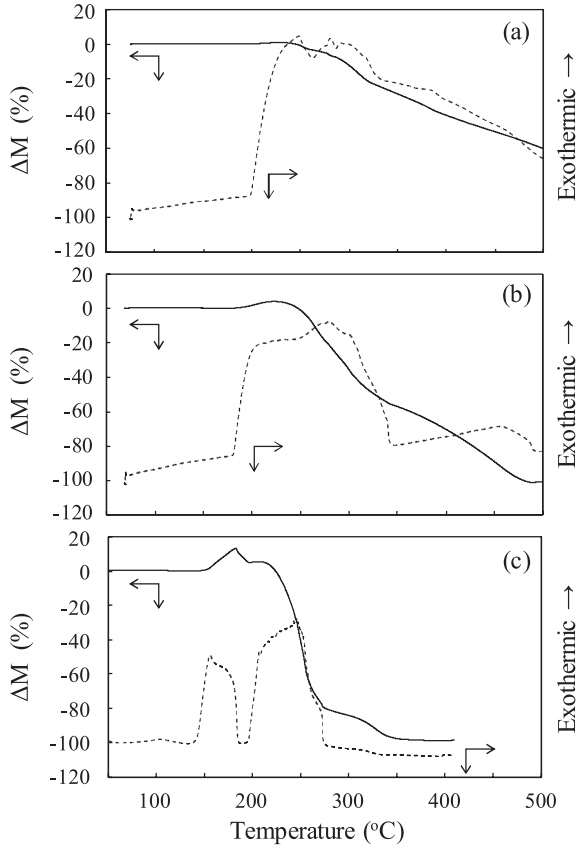

Fig. 1. TG-DTA curves of the fluorination experiment of antimony metal at three heating rates: (a) 10 °C/min, (b) 5 °C/min, and (c) 2 °C/min.

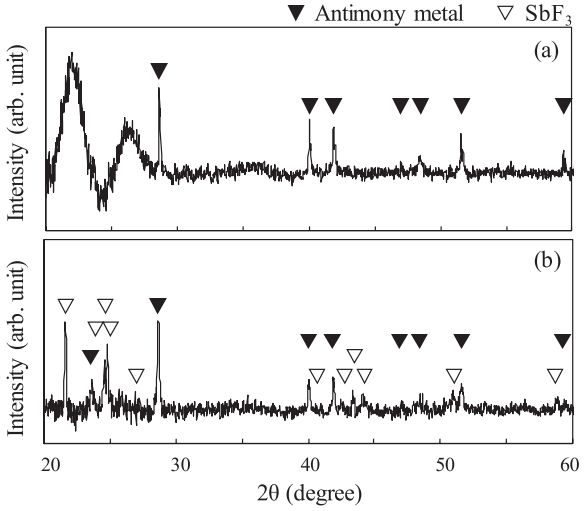

Fig. 2. XRD patterns of the residue for the fluorination experiment of antimony metal.
(a) product after fluorination at 500 °C and (b) product after fluorination at 170 °C.

In order to investigate the fluorination reaction, XRD analysis of fluorination products was carried out. Additional fluorination experiments were carried out to prepare the residue of fluorination reaction. Fig. 2(a) shows XRD pattern of the residue obtained by the fluorination experiment; the temperature was raised from room temperature to 500 °C with the heating rate of 10 °C/min. The residue was identified as antimony metal. In this figure, broad peaks corresponding to polyimide film also appeared in the 2θ range from 20 to 28 degrees. In order to