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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<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>4</sub>, and Sb<sub>2</sub>O<sub>5</sub>. The fluorination reaction of antimony metal started at 150 °C, and the fluorination product was SbF<sub>3</sub>. SbF<sub>3</sub> volatilized completely by the reaction with  $F_2$  above 190 °C; it was considered that volatile SbF<sub>5</sub> was formed by the reaction with  $F_2$ . In the series of fluorination of the antimony oxides, Sb<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>4</sub>, and Sb<sub>2</sub>O<sub>5</sub>, they started to react with  $F_2$  and volatilize at 330 °C as SbF<sub>5</sub>. During the fluorination reaction of a part of Sb<sub>2</sub>O<sub>3</sub> would oxidize remained Sb<sub>2</sub>O<sub>3</sub> to Sb<sub>2</sub>O<sub>4</sub>. 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 F2, NF3, ClF3, 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<sub>6</sub> and PuF<sub>6</sub> gases; however, PuF<sub>6</sub> is thermodynamically unstable and gradually decompose to PuF<sub>4</sub> solid [11]. On the other hand, fluorinated fission products (FPs) such as SrF2 and LaF3 have low vapor pressure, therefore, these are recovered as solid components and separated from UF<sub>6</sub> gas. Although, some FPs forms volatile fluorides and co-volatilized with UF<sub>6</sub> 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<sub>5</sub> which vapor pressure is 100 kPa at 142.7 °C [1]. Therefore, antimony may volatilize in the fluoride volatility method if SbF<sub>5</sub> 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<sub>2</sub>F, and SbOF<sub>3</sub>. 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<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>4</sub>, and Sb<sub>2</sub>O<sub>5</sub>, were used as target compounds for fluorination. Additionally, in order to well understand the fluorination reaction of the antimony compounds, fluorination of SbF<sub>3</sub>, 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 ( $\Delta$ M) 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 F2 exothermically, and antimony metal was temporarily converted to heavier compounds by reaction with F2 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 F2 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, ∆M 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)  $10^{\circ}$ C/min, (b)  $5^{\circ}$ C/min, and (c)  $2^{\circ}$ C/min.



Fig. 2. XRD patterns of the residue for the fluorination experiment of antimony metal.

(a) product after fluorination at 500  $^\circ C$  and (b) product after fluorination at 170  $^\circ C.$ 

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 2 $\theta$  range from 20 to 28 degrees. In order to



**Fig. 3.** TG-DTA curves of the fluorination experiment of  $SbF_3$  at three heating rates: (a) 10 °C/min, (b) 5 °C/min, and (c) 2 °C/min.

identify the product of the first exothermic reaction in Fig. 1(c), the residue was obtained by the fluorination experiment; the temperature was increased from room temperature to 170 °C with the heating rate of 10 °C/min followed by keeping at 170 °C for 30 min. Fig. 2(b) shows the XRD pattern of the residue obtained by this fluorination experiment. That material was identified as a mixture of antimony metal and SbF<sub>3</sub>.

#### 2.1.2. Results of fluorination experiment of SbF<sub>3</sub>

In order to further investigate the fluorination reaction of antimony metal, the fluorination experiment of SbF<sub>3</sub>, which was the intermediate fluorination product of antimony metal, was carried out. The TG-DTA curves of fluorination experiment of SbF<sub>3</sub> are shown in Fig. 3. Heating rates for Fig. 1 (a)–(c) was 10, 5, and 2 °C/min, respectively. In order to compare the reaction with F<sub>2</sub>, the TG-DTA curve of the heating experiment of SbF<sub>3</sub> at Ar atmosphere is also shown in Fig. 4.

As shown in Fig. 4,  $SbF_3$  started to volatilize at 200 °C in Ar with an endothermic reaction and the volatilization of  $SbF_3$  was completed by



280 °C. Melting point of SbF3 is 287 °C [14], and the vapor pressure of SbF<sub>3</sub> was 0.5 kPa at 200 °C and 23.3 kPa at 287 °C [14]. Because of this vapor pressure of SbF<sub>3</sub>, it was considered that SbF<sub>3</sub> started to volatilize at 200 °C and completely volatilized by 280 °C in Ar flow condition. On the other hand, in F2, exothermic peaks were observed and SbF3 volatilized completely as shown in Fig. 3. These results indicate that SbF<sub>3</sub> reacted with F<sub>2</sub> exothermically. On the other hand, DTA curves in Fig. 3 were very complicated. As same as the fluorination experiment of antimony metal, a continuous exothermic peak was separated by slowing down the heating rate. For example, the shoulder of the exothermic peak around 150 °C in Fig. 3(a) was clearly separated at 150 °C in Fig. 3(b) at a heating rate of 5 °C/min. Since  $\Delta M$  started to decrease with the exothermic peaks around 200 °C in Fig. 3, it was considered that this reaction was main fluorination reaction of SbF<sub>3</sub>. Additional  $\Delta M$ decrease was observed above 330 °C in Fig. 3 as with the fluorination experiment of antimony metal.

# 2.1.3. Results of fluorination experiment of Sb<sub>2</sub>O<sub>5</sub>

Next, the results of fluorination experiment were shown for antimony oxides. First, the result of fluorination experiment was shown for Sb<sub>2</sub>O<sub>5</sub> due to its simplest fluorination reaction. The TG-DTA curves of fluorination experiment of Sb<sub>2</sub>O<sub>5</sub> are shown in Fig. 5. Heating rates for Fig. 5(a) and (b) was 10 and 5 °C/min, respectively. As shown Fig. 5,  $\Delta$ M decreased with the exothermic reaction above 330 °C. Therefore, it was clarified that Sb<sub>2</sub>O<sub>5</sub> reacted with F<sub>2</sub> above 330 °C. Since the shapes of TG-DTA curves in Fig. 5(a) and (b) was resembled each other, the fluorination reaction would not be affected by the heating rate.

When the residue of the fluorination experiment of  $Sb_2O_5$  heated up to 500 °C with the 10 °C/min of heating rate was investigated by XRD analysis, no XRD peak was observed. As the result, it is clarified that the residue was changed from the starting material of  $Sb_2O_5$ , but it could not be identified. The physical appearance of residue was white powder which resembled the starting material of  $Sb_2O_5$ .

# 2.1.4. Results of fluorination experiment of Sb<sub>2</sub>O<sub>4</sub>

The TG-DTA curves of fluorination experiment of  $Sb_2O_4$  are shown in Fig. 6. The heating rates for Fig. 6(a) and (b) was 10 and 5 °C/min, respectively. As shown in Fig. 6, the exothermic reaction started at 330 °C, and the  $\Delta M$  decreased with the exothermic reaction. The change of exothermic peak was observed at about 430 °C. The temperature of exothermic peak around 430 °C was slightly shifted to higher



Fig. 5. TG-DTA curves of the fluorination experiment of  $Sb_2O_5$  at two heating rates: (a) 10 °C/min and (b) 5 °C/min.



Fig. 6. TG-DTA curves of the fluorination experiment of  $Sb_2O_4$  at two heating rates: (a) 10 °C/min and (b) 5 °C/min.

temperature with increasing heating rate, therefore, reaction rate would be slow compared with heating rate. However, since the shape of TG-DTA curves in Fig. 6(a) and (b) was resembled each other, the fluorination reaction would not be affected by the heating rate.

The residue of the fluorination experiment heated to 500 °C with the heating rate of 10 °C/min was identified as  $\rm Sb_2O_4$  by XRD analysis. It indicated that  $\rm Sb_2O_4$  was directly fluorinated to volatile antimony fluoride.

#### 2.1.5. Results of fluorination experiment of Sb<sub>2</sub>O<sub>3</sub>

Finally, the result of fluorination experiment was shown for Sb<sub>2</sub>O<sub>3</sub> which has the lowest valence state of antimony among the antimony oxides used in this study. The TG-DTA curves of fluorination experiment of Sb<sub>2</sub>O<sub>3</sub> are shown in Fig. 7. Heating rates for Fig. 7(a)-(c) was 10, 5, and 2 °C/min, respectively. As shown in Fig. 7, an initial sharp exothermic peak was observed around 330 °C independent of heating rate, and  $\Delta M$  started to decrease. After that,  $\Delta M$  continued to decrease with the broad exothermic curve. Therefore, it is clarified that Sb<sub>2</sub>O<sub>3</sub> reacted with F2 above 330 °C by two step reactions. In the case of 2 °C/ min of heating rate (Fig. 7(c)), all of the  $Sb_2O_3$  was volatilized. On the other hand, some amount of material remained after the fluorination experiment in the case of 10 and 5 °C/min. It would be caused by difference of the F<sub>2</sub> feed time in each experiment; this effect was mentioned in Section 2.1.1 in detail. Since the shape of TG-DTA curves in Fig. 7(a), (b), and (c) was resembled each other, the fluorination reaction would not be affected by the heating rate.

The residue after the fluorination of Sb<sub>2</sub>O<sub>3</sub> heated up to 500 °C with a heating rate of 10 °C/min was identified as Sb<sub>2</sub>O<sub>4</sub> by XRD analysis. It indicated that Sb<sub>2</sub>O<sub>3</sub> was converted to Sb<sub>2</sub>O<sub>4</sub> in the course of the fluorination reaction.

# 2.2. Thermodynamic consideration of fluorination of antimony compounds

In this section, thermodynamic consideration was examined for related reaction of fluorination reaction of antimony compounds. The Gibbs free energy ( $\Delta$ G) for the related reactions were evaluated by the calculation using the thermodynamic data base [16] and using the thermodynamic properties which Wagman et al. [17] suggested. The results of thermodynamic consideration are shown in Fig. 8. Since the data of SbF<sub>5</sub> and oxyfluorides except for SbOF were missing, the related reactions were not given in Fig. 8.



Fig. 7. TG-DTA curves of the fluorination experiment of  $Sb_2O_3$  at three heating rates: (a) 10 °C/min, (b) 5 °C/min, and (c) 2 °C/min.



Fig. 8. Gibbs free energy of the reaction of antimony compounds.

Fluorination reactions of antimony metal and Sb<sub>2</sub>O<sub>3</sub> were negative  $\Delta G$  value in the temperature range as given in Fig. 8. In room temperature,  $\Delta G$  of the fluorination reaction forming SbOF from Sb<sub>2</sub>O<sub>3</sub> was negative, however,  $\Delta G$  of the fluorination reaction forming SbF<sub>3</sub> from SbOF also was negative. Therefore, if SbOF was formed by the fluorination reaction, it would be further fluorinated to SbF<sub>3</sub>. As mentioned in Section 2.1.5, Sb<sub>2</sub>O<sub>4</sub> was formed in the fluorination experiment of Sb<sub>2</sub>O<sub>3</sub>. It was indicated in Fig. 8 that Sb<sub>2</sub>O<sub>3</sub> would be oxidized to Sb<sub>2</sub>O<sub>4</sub> by the reaction with O<sub>2</sub>.

#### 2.3. Fluorination reaction of antimony compounds

#### 2.3.1. Fluorination reaction of antimony metal

As mentioned in Section 2.1.1, three reactions were observed in the TG-DTA curves shown in Fig. 1; exothermic reaction with mass increase at 150 °C, exothermic reaction with mass decrease at 190 °C, and reaction with slight mass decrease at 330 °C. These reactions were clearly observed in Fig. 1(c) because the fluorination reactions could be separately observed at slow heating rate. And as shown in Fig. 2, the residue of fluorination reaction at 500 °C was antimony metal, and that at 170 °C was antimony metal and SbF<sub>3</sub>. Based on these result, it is confirmed that fluorination reaction of antimony metal at 150 °C and 190 °C were described by reactions (1) and (2).

$$2/3Sb + F_2 \rightarrow 2/3SbF_3 \tag{1}$$

$$SbF_3 + F_2 \rightarrow SbF_5$$
 (2)

As shown in Fig. 3, the fluorination reaction of  $SbF_3$  with drastic decrease of  $\Delta M$  was observed at 190 °C which was same temperature of second exothermic reaction shown in Fig. 1(c). This result would be support the idea that the exothermic reaction at 190 °C in Fig. 1 was reaction (2).

The vapor pressure of  $SbF_3$  was evaluated as about  $10^{-1}$  kPa at 150 °C by the calculation using a thermodynamic data base [16], and that of SbF<sub>5</sub> has been reported as 100 kPa at 142.7 °C [1]. Namely, SbF<sub>3</sub> has low volatility at 150 °C, and SbF5 has high volatility at that temperature. And in 150 °C, SbF3 did not volatilize as shown in Fig. 4. Therefore, the temporary increase of  $\Delta M$  at 150 °C in Fig. 1(c) would be caused by the formation of SbF<sub>3</sub>. Then,  $\Delta M$  should be +47% when reaction (1) completed without volatilization of SbF<sub>3</sub>. However,  $\Delta M$ was +13% as maximum in Fig. 1(c). From this view point, in Fig. 1(c), metal antimony would be remained at 180 °C which was finish temperature of initial fluorination reaction. On the other hand,  $\Delta M$  started to decrease above 180 °C in Fig. 1(c). At 180 °C, vapor pressure of SbF<sub>3</sub> was 0.2 kPa [16], and SbF<sub>3</sub> did not volatilize as shown in Fig. 4. Since fluorination reaction was large exothermic reaction, temperature of local place such as the interface of gas-solid reaction may be increased over 180 °C in this experiment. Because of this reason, antimony metal started to volatilize at 180 °C as SbF3 or SbF5. After the fluorination of SbF<sub>3</sub> started above 190 °C, decrease of  $\Delta M$  stopped from 190 °C to 220 °C in Fig. 1(c). As mentioned in more detail section 2.3.2, it would be caused by balancing of volatilization of SbF5 and formation of addition compounds consisted by SbF<sub>3</sub> and SbF<sub>5</sub>, which was suggested by Colbin [14].

In the XRD pattern of residue of fluorination reaction of antimony metal at 500 °C shown in Fig. 2(a), only antimony metal peaks were detected.  $SbF_3$  was fluorinated to volatile  $SbF_5$  above 190 °C. It indicates that metal antimony would be fluorinated to  $SbF_5$  directly above 190 °C. Therefore, it was considered that  $SbF_3$  peaks were not detected and only antimony metal peaks were detected in the XRD pattern of Fig. 2(a).

In Fig. 1(c),  $\Delta M$  slightly decreased over 330 °C. As shown in Figs. 5–7, antimony oxides started to react with F<sub>2</sub> above 330 °C. The XRD pattern of starting material of antimony metal indicated only antimony metal, however, the surface of starting material may be already oxidized. Since the decrease of  $\Delta M$  was slight at 330 °C in Fig. 1(c), it was considered that the reaction would be fluorination reaction of antimony oxide such as oxidized surface of antimony metal.

In TG-DTA curves in Fig. 1, exothermic peaks were not separately observed each other at high heating rate, however, the shape of TG-DTA curves were seemed to be resembled. It is considered that heating rate would not affect to the fluorination reaction of antimony metal.

#### 2.3.2. Fluorination reaction of $SbF_3$

As shown in Fig. 3, several exothermic peaks were observed in the TG-DTA curves. However, the exothermic reaction with drastic

decrease of  $\Delta M$  was observed above 190 °C especially; decrease of  $\Delta M$  seemed to be delayed from start of the exothermic reaction. Therefore, it was considered as main fluorination reaction of SbF<sub>3</sub>, which was given as reaction (2), was exothermic peaks above 190 °C.

The shoulder of the exothermic peak at 150 °C in Fig. 3(a) and the exothermic peak at 150 °C in Fig. 3(b) was observed with or without slightly mass increase; this exothermic peak was obscure for Fig. 3(c). Colbin [14] suggested some addition compounds consisted by SbF<sub>3</sub> and SbF<sub>5</sub>. Since the change of  $\Delta M$  was small, exothermic reaction may fluorination reaction to produce such addition compounds.

In main fluorination reaction above 190 °C, two or three exothermic peaks was observed in Fig. 3 (c). Since the heat production was large in the fluorination reaction because the valence state of antimony was oxidized to pentavalent from trivalent, the temperature may be increased locally by heat production of the fluorination reaction as same as the fluorination reaction of antimony metal. In such condition, fluorination of SbF<sub>3</sub> and volatilization of SbF<sub>3</sub> and SbF<sub>5</sub> would be concurrently occurred; it meant that some phenomena were concurrently occurred. Because of these phenomena, it may be considered that some sharp exothermic peaks were found above 190 °C in Fig. 3. Additionally, decrease of  $\Delta$ M was delayed from start of the exothermic reaction around 190 °C, this may be caused by balancing of volatilization of SbF<sub>5</sub> and formation of addition compounds, which was mentioned in previous paragraph.

As same as the case of antimony metal,  $\Delta M$  seemed to decrease slightly over 330 °C in Fig. 3. It would be caused by fluorination reaction of few amount of antimony oxide. And, in TG-DTA curves in Fig. 3, exothermic peaks were not separately observed each other at high heating rate, however, the shape of TG-DTA curves were seemed to be resembled. It is considered that heating rate would not affect to the fluorination reaction of SbF<sub>3</sub>.

#### 2.3.3. Fluorination reaction of $Sb_2O_5$

 $Sb_2O_5$  was volatilized by the fluorination reaction above 330 °C as shown in Fig. 5. Since antimony is pentavalent in  $Sb_2O_5$ , antimony cannot be further oxidized to a higher valence state even by the fluorination reaction. Reduction of antimony also cannot occur by the fluorination reaction. Therefore, the fluorination reaction is considered as reaction (3).

$$1/5Sb_2O_5 + F_2 \rightarrow 2/5SbF_5 + 1/2O_2$$
 (3)

As mentioned in section 1, formation of oxyfluoride should be investigated for the fluorination reaction of oxide materials. Colbin [14] suggested antimony oxyfluorides such as  $SbO_2F$ , and  $SbOF_3$ . The decomposition reactions of antimony oxyfluorides were suggested as reactions (4) and (5) [14].

$$5SbO_2F \rightarrow 2Sb_2O_4 + SbF_5 + O_2 \tag{4}$$

$$5SbOF_3 \rightarrow Sb_2O_4 + 3SbF_5 + 1/2O_2$$
 (5)

The reaction temperatures of reactions (4) and (5) were reported as  $350 \,^{\circ}\text{C}$  and  $200 \,^{\circ}\text{C}$ , respectively [14].  $\text{SbO}_2\text{F}$  seemed to be relatively stable at  $330 \,^{\circ}\text{C}$  which was the reaction temperature of the fluorination of  $\text{Sb}_2\text{O}_5$ . Therefore,  $\text{SbO}_2\text{F}$  was considered as a potential intermediate.  $\text{Sb}_2\text{O}_5$  may be fluorinated to  $\text{SbF}_5$  via  $\text{SbO}_2\text{F}$  according to reactions (6) and (7).

$$Sb_2O_5 + F_2 \rightarrow 2SbO_2F + 1/2O_2$$
 (6)

$$1/2SbO_2F + F_2 \rightarrow 1/2SbF_5 + 1/2O_2$$
 (7)

However, the TG-DTA curve was looked as that  $Sb_2O_5$  was reacted by one step reaction. Therefore, if  $SbO_2F$  were formed by reaction (6),  $SbO_2F$  would be immediately fluorinated to  $SbF_5$  by reaction (7).

The residue of fluorination reaction of  $Sb_2O_5$  could not be identified. The residue of fluorination experiment of  $Sb_2O_3$  and  $Sb_2O_4$  was oxide compound, which was  $Sb_2O_4$ . Abe et al. [18] suggested amorphous  $Sb_2O_5$ . The residue of fluorination reaction of  $Sb_2O_5$  may be amorphous oxide such as amorphous  $Sb_2O_5$ .

# 2.3.4. Fluorination reaction of Sb<sub>2</sub>O<sub>4</sub>

As shown in the TG-DTA curves in Fig. 6, Sb<sub>2</sub>O<sub>4</sub> started to react with F<sub>2</sub> above 330 °C. The residue of fluorination reaction was starting material of Sb<sub>2</sub>O<sub>4</sub>. It suggested that Sb<sub>2</sub>O<sub>4</sub> was directly fluorinated to volatile compound. On the other hand, Sb<sub>2</sub>O<sub>4</sub> was reported as a mixture of trivalent and pentavalent antimony [19]. It would suggest that Sb<sub>2</sub>O<sub>4</sub> was consisted by Sb<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>5</sub>. Therefore, it was considered that Sb<sub>2</sub>O<sub>4</sub> was fluorinated by reactions (3) and (8).

$$1/5Sb_2O_3 + F_2 \rightarrow 2/5SbF_5 + 3/10O_2$$
 (8)

As shown in Fig. 7, the fluorination reaction of Sb<sub>2</sub>O<sub>3</sub> proceeded by two step reactions; sharp exothermic reaction with  $\Delta M$  decrease and broad exothermic reaction with  $\Delta M$  decrease. The sharp exothermic reaction was not observed in the fluorination reaction of Sb<sub>2</sub>O<sub>5</sub> as shown in Fig. 5. Therefore, sharp exothermic peak would be caused by the change of the valence state of antimony. Because of this reason, the change in the exothermic peak around 430 °C in the Fig. 6 was considered to be caused by the change of the valence state of antimony in the Sb<sub>2</sub>O<sub>4</sub> from trivalent to pentavalent. On the other hand, the sharp exothermic peak at 330 °C observed in the fluorination reaction of Sb<sub>2</sub>O<sub>3</sub> (Fig. 7) was not observed in Fig. 6. When Sb<sub>2</sub>O<sub>4</sub> was used as starting material, it is considered that the fluorination of Sb<sub>2</sub>O<sub>3</sub> started at 330 °C by reaction (3) first, and the fluorination of Sb<sub>2</sub>O<sub>3</sub> started by reaction (8) later.

#### 2.3.5. Fluorination reaction of Sb<sub>2</sub>O<sub>3</sub>

As mentioned in Section 2.1.5, Sb<sub>2</sub>O<sub>3</sub> reacted with F<sub>2</sub> above 330 °C by two step reactions shown in the TG-DTA curves in Fig. 7; sharp exothermic reaction with  $\Delta M$  decrease and broad exothermic reaction with  $\Delta M$  decrease. And, the residue of the fluorination reaction was identified as Sb<sub>2</sub>O<sub>4</sub> by XRD analysis. Sb<sub>2</sub>O<sub>3</sub> was volatilized by the fluorination reaction as shown in Fig. 7, therefore, the fluorination reaction was considered as reaction (8). SbOF and SbF<sub>3</sub> would be potential product of fluorination reaction, however,  $\Delta G$  of fluorination reaction of SbOF to SbF<sub>3</sub> awas negative as shown in Fig. 8 and SbF<sub>3</sub> should fluorinated to SbF<sub>5</sub> above 190 °C as discussed in Sections 2.3.1 and 2.3.2. Therefore, reaction (8) was considered as appropriate fluorination reaction.

On the other hand, since  $Sb_2O_4$  was formed in the experiment, oxidation reaction (9) also would be occurred concurrently.

$$2Sb_2O_3 + O_2 \rightarrow 2Sb_2O_4 \tag{9}$$

Reactions (8) and (9) are summarized as reaction (10).

$$4/5Sb_2O_3 + F_2 \rightarrow 2/5SbF_5 + 3/5Sb_2O_4 \tag{10}$$

If all of the Sb<sub>2</sub>O<sub>3</sub> is converted to Sb<sub>2</sub>O<sub>4</sub> according to reaction (10),  $\Delta$ M should become -20%. In Fig. 7(a)–(c),  $\Delta$ M was about -15, -13, and -7% at the end of the sharp exothermic peak, respectively; the  $\Delta$ M values were obtained at 430, 390, and 370 °C for Fig. 7(a)–(c), respectively. These  $\Delta$ M values were near to -20%. Antimony is oxidized to higher valence state in reactions (8) and (9), so the reaction heat should be a high value. Therefore, the reaction with sharp exothermic peak at 330 °C was considered as reactions (8) and (9). And broad exothermic reaction was resembled to TG-DTA curve of Sb<sub>2</sub>O<sub>4</sub>, therefore, broad exothermic peak in Fig. 7 would be fluorination reaction of Sb<sub>2</sub>O<sub>4</sub>.

#### 3. Conclusion

The reactions of antimony metal, fluoride and oxides with  $F_2$  were investigated by TG-DTA analyses and XRD analysis. Antimony metal was fluorinated to SbF<sub>3</sub> above 150 °C. SbF<sub>3</sub> reacted with  $F_2$  and completely volatilized above 190 °C, therefore, SbF<sub>5</sub> would be formed by

the reaction.  $Sb_2O_5$  reacted with  $F_2$  and volatilized above 330 °C.  $Sb_2O_3$  reacted with  $F_2$  and completely volatilized finally above 330 °C, however,  $Sb_2O_4$  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  $Sb_2O_4$ .  $Sb_2O_4$ , reported as a mixture of trivalent and pentavalent antimony, reacted with  $F_2$  and volatilized above 330 °C. The product of the fluorination reactions of these antimony oxides was considered as volatile  $SbF_5$ . Therefore, it was clarified that antimony compounds reacted with fluorine and antimony would be volatilized as  $SbF_5$  by the fluorination reaction.

### 4. Experimental

#### 4.1. Materials

Antimony metal of 99.5% purity, SbF<sub>3</sub> of 95% purity, Sb<sub>2</sub>O<sub>5</sub> (the purity was not provided) (all form Wako Pure Chemical Industries, Ltd.), and Sb<sub>2</sub>O<sub>3</sub> of 99.995% purity (Sigma-Aldrich Co., LLC) were used as-received. Sb<sub>2</sub>O<sub>4</sub> was obtained by the oxidation of Sb<sub>2</sub>O<sub>3</sub> in air at 900 °C and its identity verified by XRD analysis. All of the antimony compounds including antimony metal were fine powder. Analytical grade 5% F<sub>2</sub>-N<sub>2</sub> gas (95.09% N<sub>2</sub> and 4.91% F<sub>2</sub>) and 10% F<sub>2</sub>-N<sub>2</sub> (90.1% N<sub>2</sub> and 9.9% F<sub>2</sub>) (Central Glass Co., Ltd.,) and argon gas of 99.9999% purity (Nippon Sanso Co., Ltd.) were used as-received; the study was started with 5% F<sub>2</sub>-N<sub>2</sub> but when it could not be obtained, 10% F<sub>2</sub>-N<sub>2</sub> was used for the remaining experimental runs.

#### 4.2. Thermogravimetric and differential thermal analyses

The Rigaku TG-DTA system (Thermo plus 2) set in a high purity argon atmosphere glove box was used. In order to prevent corrosion by  $F_2$ , nickel or nickel alloy was used in the TG-DTA system and the pan for the TG-DTA. The amount of antimony compounds for an experimental run was about 10 mg. The flow gas was a mixture of Ar (40 mL/min) and 5%  $F_2$ -N<sub>2</sub> (20 mL/min) or a mixture of Ar (50 mL/min) of and 10%  $F_2$ -N<sub>2</sub> (10 mL/min).  $F_2$  in off-gas was eliminated by an adsorption method using Al<sub>2</sub>O<sub>3</sub> adsorbent. Heating was carried out from room temperature to 500 °C with heating rates of 2, 5, and 10 °C/min.

#### 4.3. X-ray diffraction analysis

The identification of the residue of the fluorination experiment was carried out by X-ray powder diffraction with the Rigaku X-ray diffractometer (MiniFlex600). The sample material for XRD analysis was covered as necessary by polyimide film to prevent exposure to air.

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