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Mechanism of stibnite volatilization at high temperature

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Abstract: The volatilization of stibnite (Sb_2S_3) in nitrogen from 700 to 1000 °C was investigated by using thermogravimetric analysis. The results indicate that in inert atmosphere, stibnite can be volatilized most efficiently as Sb_2S_3 (g) at a linear rate below 850 °C, with activation energy of 137.18 kJ/mol, and the reaction rate constant can be expressed as $k=206901\exp(-16.5/T)$. Stibnite can be decomposed into Sb and sulfur at temperature above 850 °C in a nitrogen atmosphere. However, in the presence of oxygen, stibnite is oxidized into Sb and SO_2 gas at high temperature. Otherwise, Sb is oxidized quickly into antimony oxides such as Sb_2O_3 and SbO_2, while Sb_2O_3 can be volatilized efficiently at high temperature.

Key words: stibnite; volatilization; nitrogen; thermogravimetric analysis

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1 Introduction

The global supply of antimony comes mainly from the sulphide mineral stibnite (Sb_2S_3), and partially from oxidized ores such as cervantite ($Sb_2O_3 \cdot Sb_2O_5$). The major deposits of antimony ore are located in Bolivia, South Africa, Mexico and China, while the Hunan district in South China is normally the largest producer [1−5].

Pyro-metallurgical methods are generally used for production of antimony, but wet and electrical operations are also applied for certain types of ores [2, 6−7]. The methods for recovery of antimony can be generally classified into three types: 1) production of the trioxide via volatilization roast followed by reduction to metal, 2) direct production from ore by reverberatory, blast and special furnace methods [8−9], and 3) electrolysis of a solution containing the metal in sodium sulphide [10−13]. Volatilization roasting−reduction smelting is mainly used to produce antimony from sulfide ores and concentrates. In this process, antimony sulphide is volatilized and then oxidized into antimony trioxide (Sb_2O_3) in a rotary kiln of a shaft furnace. Finally, Sb_2O_3 is reduced to antimony by carbon in a reverberatory furnace. The related reactions can be described as

$$2Sb_2S_3+9O_2 \rightarrow 2Sb_2O_3+6SO_2 \qquad (1)$$

$$Sb_2O_3+3C \rightarrow 2Sb+3CO \qquad (2)$$
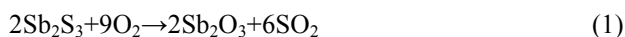
This process has been widely employed in the antimony industry [6−7, 14]. However, reports on the production of antimony from sulfides have focused little on the rate of oxidation/volatilization of stibnite. For the oxidation of synthetic Sb_2S_3, a nonisothermal study on the reaction of Sb_2S_3 in air from 473 to 1073 K (200 to 800 °C) [15] showed that the oxidation proceeds according to Eq. (1), and the oxidation reaction of Sb_2S_3 takes place in kinetic region, implying that reaction surface and temperature will limit the reaction rate:

$$Sb_2O_3+O_2 \rightarrow 2SbO_2 \qquad (3)$$

HUA et al [16] studied the volatilization of Sb_2S_3 in a steam atmosphere from 923 to 1123 K (650 to 850 °C), and they proposed a complex gas phase reaction mechanism that Sb_2S_3 could be oxidized/decomposed by water vapor to Sb_2O_3 and metallic Sb at high temperature.

Knowledge of the behaviors of Sb_2S_3 at high temperatures (i.e. rate of decomposition and/or volatilization) in inert and oxidizing atmospheres is of great importance for control of antimony and its compounds in antimony smelting, or in other non-ferrous smelting, so as to eliminate impure antimony components.

In this work, the oxidation/volatilization of stibnite in nitrogen−oxygen atmosphere is focused on.

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2 Materials and methods

2.1 Materials

The material of Sb_2S_3 was obtained from Aladdin Industrial Co. (Shanghai, China) and was a fine powder with 98% Sb_2S_3. Nitrogen (with purity of 99%) and air (79% N_2 and 21% O_2) were procured from local suppliers. The powder of Sb_2S_3 was analyzed by X-ray diffraction (XRD). The XRD result of Sb_2S_3 is shown in Fig. 1.
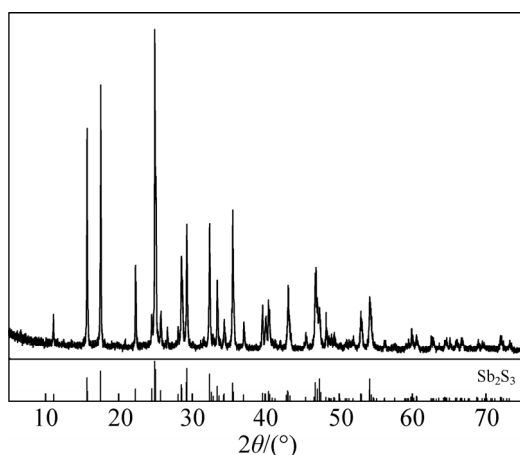

Fig. 1 XRD pattern of Sb_2S_3

2.2 Methods

Most experiments were carried out in a thermogravimetric analysis (TGA) apparatus (STA449 F3, NETZSCH) which essentially consisted of a high-temperature vertical tube furnace, an electronic balance connected to a personal computer (PC) for continuously recording the mass variation, and a gas delivery system. The powder sample was weighed using an electronic balance with an accuracy of 1×10^{-4} g, placed in a 3 mL ceramic crucible (alumina and porcelain); the samples were suspended from the balance by a quartz chain in the tube reactor, and the instantaneous mass loss was recorded as a function of time. The nonisothermal experiments were performed at a heating rate of 10 °C/min and an argon flow rate of 100 mL/min. The isothermal experiments were performed in the temperature range of 650−900 °C at a heating rate of 30 °C/min and an argon flow rate of 100 mL/min. Additionally, in some experiments carried out in a muffle furnace, nitrogen and air (3 L/min, 101 kPa) were used to determine the physical-chemical processes that occur when stibnite samples were heated under different conditions. The samples were analyzed by XRD (Germany Bruker-axs D8 Advance, Cu K_α radiation, $\lambda=$ 1.5406 Å).

3 Results and discussion

3.1 Thermodynamics in Sb-S-O system

The data of Gibbs free energy of formation from HSC Chemistry (v 6.0) database that pertain to the relevant compounds in the Sb-S-O system were reviewed critically and compared with various available sources. HSC was used to calculate the relationship between ΔG and temperature of antimony oxidation. Figure 2 shows that antimony oxidation occurs spontaneously even at low temperature because the ΔG is less than 0. Therefore, it can be concluded that Sb_2S_3 can be oxidized to Sb, Sb_2O_3, SbO_2, or $Sb_2(SO_4)_3$ at temperature lower than 1200 °C. HSC was used to plot predominance diagrams of the Sb-S-O system. These diagrams are useful in predicting the stability conditions for mineral species in contact with vapor phases, as in the case of roasting and smelting. Thus, an isothermal diagram for the Sb-S-O system is shown in Fig. 3, where predominance areas are shown for condensed phases in equilibrium with vapor phase at 900, 1100 and 1300 °C as a function of the
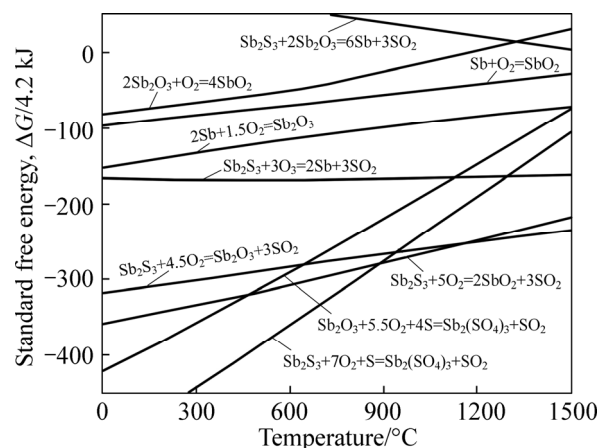

Fig. 2 Relationship between ΔG and temperature of antimony oxidation

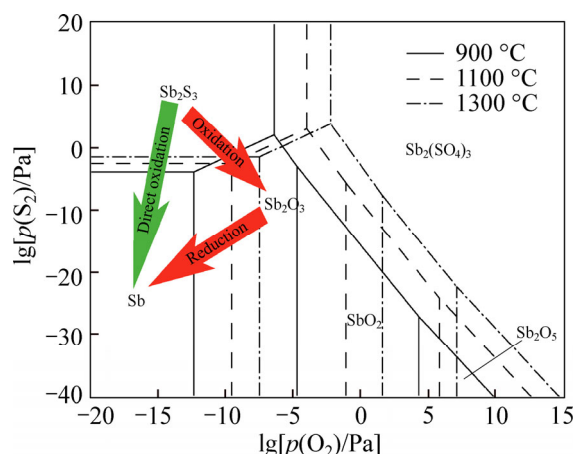**Fig. 3** Stability diagram for Sb-S-O system at 900 °C, 1100 °C and 1300 °C

partial pressures of S_2 and O_2 (marked as $p(S_2)$ and $p(O_2)$, respectively). This equilibrium diagram indicates that Sb_2S_3 in the presence of oxygen is first oxidized to Sb_2O_3 as an intermediate, and then, under higher $p(O_2)$ and low $p(S_2)$ in the vapor, it is further oxidized to SbO_2. Generally, in traditional antimony smelting, stibnite concentrate is first oxidized to the volatile trioxide in the "Oxidation" area in Fig. 3, and the antimony trioxide is reduced to metal by a reducing agent such as charcoal or coal in the "Reduction" area. However, if the equilibrium can be attained at a high $p(S_2)$, then antimony sulfate would be the final stable antimony phase in the "Direct Oxidation" area. This is the theoretical foundation for direct production of antimony from stibnite.

Figure 4 shows the equilibrium conditions of condensed phases as a function of $p(O_2)$ and temperature, under constant $p(S_2)$ of 0.1, 10 and 100 Pa in the gas phase. This diagram indicates that Sb is a stable phase at high temperature and low $p(O_2)$. When $p(S_2)$ changes, the temperature and $p(O_2)$ change correspondingly, for example,

$p(S_2)$=0.1 Pa, t=710 °C, $\lg p(O_2)$<−16;
$p(S_2)$=10 Pa, t=890 °C, $\lg p(O_2)$<−12.5;
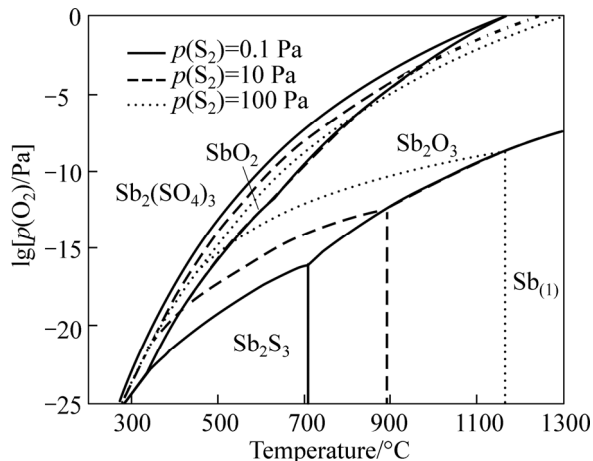$p(S_2)$=100 Pa, t=1180 °C, $\lg p(O_2)$< −9

Fig. 4 Stability diagram for Sb-S-O system as function of temperature at constant $p(S_2)$ of 0.1 Pa, 10 Pa and 100 Pa

3.2 Non-isothermal volatilization of Sb_2S_3 in nitrogen

The thermal behavior of Sb_2S_3 in a nitrogen atmosphere was studied from 150 to 1000 °C. The result is shown in Fig. 5. A smooth mass-loss curve (TG) starting at about 664 °C can be observed, indicating that a complete volatilization of Sb_2S_3 occurs without mass variation up to 900 °C. However, the differential thermal analysis (DTA) curve shows three clear endothermic peaks and one exothermic peak. The first peak at 538.1 °C is attributed to the melting of Sb_2S_3, the second peak at 772.1 °C to the volatilization of Sb_2S_3, and the
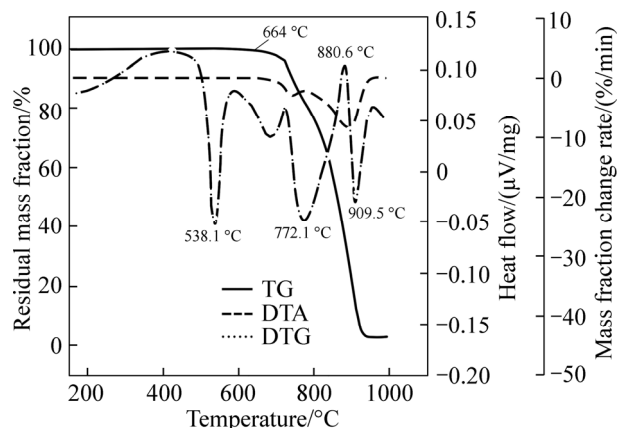

Fig. 5 Nonisothermal behavior of stibnite in nitrogen atmosphere

third peak at 909.5 °C probably to the volatilization of Sb since the rate of mass-loss (DTG) increases at about 900 °C. The exothermic peak at 880.6 °C is attributed to the decomposition of Sb_2S_3.

3.3 Isothermal volatilization of Sb_2S_3 in nitrogen

To study the effect of temperature on the antimony volatilization in nitrogen atmosphere, experiments were carried out in a TGA analyzer at constant temperature. The temperature is in the range of 700−950 °C, because this range is above the melting point of stibnite. The data are presented as the fraction of mass loss rate $((m_t−m_0)/m_0)$ as a function of time in Fig. 6, where m_t is the instantaneous mass and m_0 is the initial mass of the sample. As shown in Fig. 6, temperature has significant influence on the volatilization rate. The volatilization of stibnite in nitrogen gas is slow at 700 °C, where the mass loss fraction is only 35% after 50 min. However, the mass loss rate increases greatly at higher temperature. The stibnite is volatilized linearly with time between 700 and 850 °C. Conversely, at 900 °C, the volatilization of Sb_2S_3 not only deviates from linearity, but the slope of
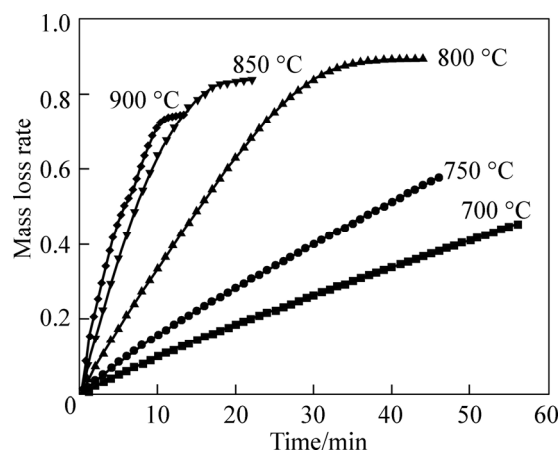

Fig. 6 Volatilization of stibnite in nitrogen atmosphere as function of temperature

the mass loss curve also suddenly changes before the mass loss maximizes. This result indicates a change in the mechanism of the volatilization as a less volatile compound is formed. To determine the nature of the mechanism, a sample is obtained at 1000 °C interrupted for 10 min and analyzed by XRD. The result is shown in Fig. 7, where the diffraction peaks for Sb_2S_3 and Sb can be detected. This result indicates that at high temperatures, decomposition of Sb_2S_3 into Sb and sulfur occurs with the volatilization of Sb_2S_3. Thus, at temperature above 850 °C, the stibnite is volatilized at a much smaller rate than at low temperature because the equilibrium partial pressure of metallic antimony is lower than that of stibnite owing to its high boiling point of 1587 °C.
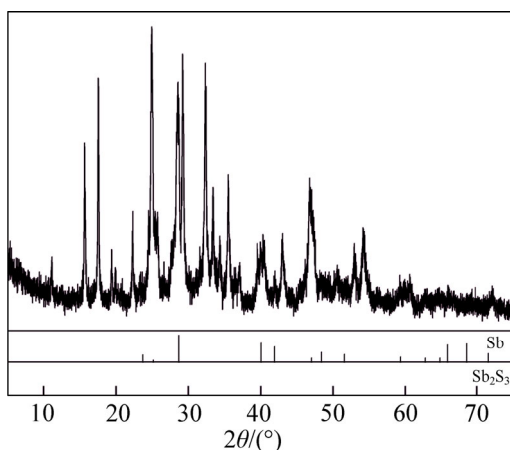

Fig. 7 XRD pattern of sample obtained at 1000 °C in volatilization of stibnite in nitrogen atmosphere

Therefore, according to the thermodynamic prediction and XRD, the mechanism of Sb_2S_3 volatilization in a nitrogen atmosphere at temperature above 850 °C can be expressed as follows:

$$Sb_2S_3(l)=Sb_2S_3(g) \tag{4}$$

$$Sb_2S_3(l)=2Sb(l)+3S_2(g) \tag{5}$$

$$Sb(l)=Sb(g) \tag{6}$$

It is assumed that the volatilization of Sb_2S_3 can be ignored, and then HSC is used to calculate the equilibrium amounts of products as a function of temperature (Fig. 8). Sb_2S_3 can be decomposed into antimony and sulfur at 760 °C, and completely decomposed at 980 °C. Figure 8 can also prove the occurrence of Reaction (5).

Nevertheless, in the region of linear volatilization (700−850 °C), from the curves $\Delta m/m_0$ vs t shown in Fig. 6, the slopes and correlation coefficients (R^2) are calculated and shown in Table 1. An Arrhenius plot is constructed by using the rate constants (Fig. 9). The slope of the fitted line shows that for the stibnite
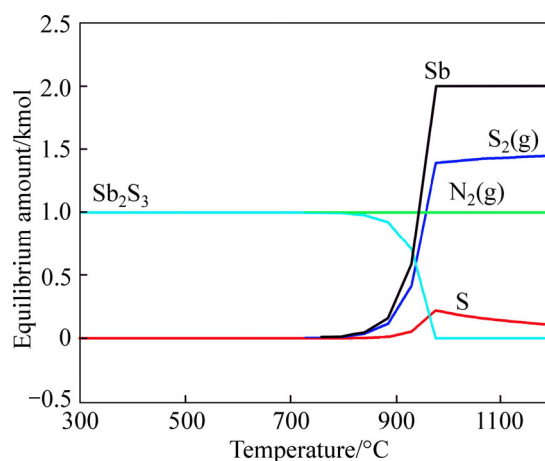

Fig. 8 Equilibrium amounts of reduced products as functions of temperature (Sb_2S_3: 1 kmol, N_2: 1 kmol)

Table 1 Slopes and correlation coefficient (R^2) for volatilization linear of stibnite in nitrogen

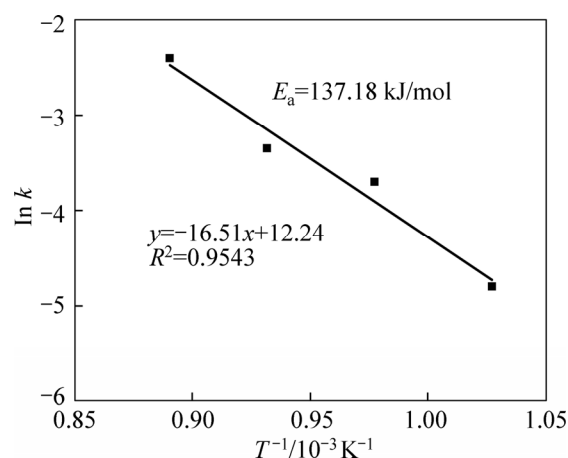| Temperature/°C	Slope	R^2
700	0.00796	0.9977
750	0.02675	0.9959
800	0.03002	0.9967
850	0.12905	0.9935

Fig. 9 Arrhenius plot for volatilization of stibnite in nitrogen atmosphere

vaporization in a nitrogen atmosphere to take place in temperature range of 700−850 °C, the activation energy of Reaction (4) is calculated to be 137.18 kJ/mol. The reaction rate constant of the Sb_2S_3 volatilization can be expressed as follows:

$$k=206901\exp(-16.5/T) \tag{7}$$

3.4 Volatilization of Sb_2S_3 in air gas

To clarify the effect of oxygen on the stibnite volatilization, experiments were carried out at 1000 °C in a muffle furnace by introducing air at different time points and then samples were collected for XRD analysis.

Figure 10 shows the XRD results for the experiments conducted at 2, 5 and 10 min, respectively. Clearly, the oxidation of stibnite is rapid at 2 min, because white smoke is formed and adheres to the furnace wall, and antimony is found, indicating that Sb_2S_3 is oxidized into antimony and antimony oxide. At 5 and 10 min, however, the peaks of antimony are weakened and the peak of antimony oxide is enhanced. Therefore, based on the XRD results, the oxidation/volatilization of Sb_2S_3 in the presence of oxygen is proposed to occur as follows:

$$Sb_2S_3+O_2(g)=Sb+SO_2(g) \tag{8}$$

$$Sb+O_2=Sb_2O_3 \tag{9}$$

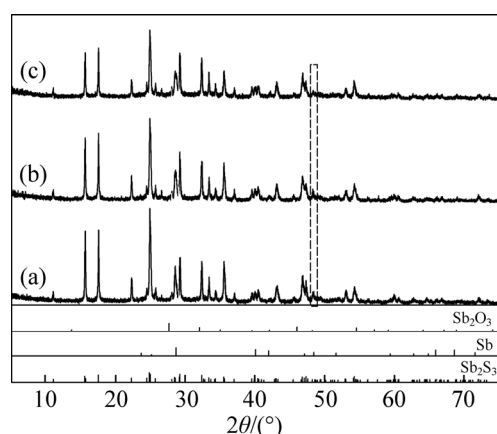$$Sb_2O_3(l)=Sb_2O_3(g) \tag{10}$$

Fig. 10 XRD patterns for volatilization at short time in air gas at 1000 °C: (a) 2 min; (b) 5 min; (c) 10 min

It is assumed that the volatilization of Sb_2S_3 can be ignored, and then HSC software is used to calculate the amounts of products under equilibrium at the molar ratio of Sb_2S_3 to O_2 of 1:3 in air as a function of temperature (Fig. 11). At temperature lower than 670 °C, Sb_2S_3 is oxidized to antimony oxides such as Sb_2O_3 and SbO_2, but antimony sulphate is not reduced. At 670 °C, Sb_2S_3
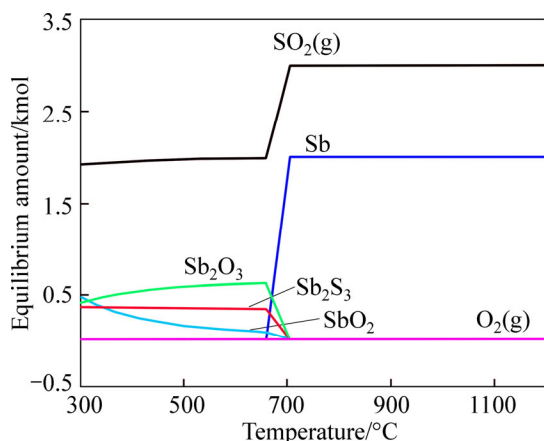

Fig. 11 Equilibrium amounts of reduced products as function of temperature (Sb_2S_3: 1 kmol, O_2: 3 kmol)

begins to be oxidized to the molten antimony. At temperature above 705 °C, Sb_2S_3 is completely decomposed into Sb and SO_2 gas. Accordingly, Sb_2S_3 is more reactive with oxygen than Sb, because there are no antimony oxides at high temperature.

4 Conclusions

1) The experimental evidence and the proposed mechanisms indicate that in an inert atmosphere, stibnite can be volatilized most efficiently as $Sb_2S_3(g)$ at about 850 °C.

2) The volatilization activation energy is 137.18 kJ/mol and the reaction rate constant can be expressed as $k=206901\exp(-16.5/T)$.

3) Stibnite decomposes to antimony and sulfur gas at above 850 °C, and the antimony vaporization is retarded, because the volatilization of metallic Sb is very slow compared with Sb_2S_3.

4) Stibnite is oxidized quickly into Sb and SO_2 gas at high temperature in the presence of oxygen, antimony is oxidized into antimony oxides such as Sb_2O_3 and SbO_2, and Sb_2O_3 can be volatilized efficiently at high temperature.

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