

EFFECT OF Na_2CO_3 ON THE PREPARATION OF METALLIC TIN FROM CASSITERITE ROASTED UNDER STRONG REDUCTIVE ATMOSPHERE

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Abstract

Tin is an indispensable metal in the modern industry. The current tin smelting processes, however, have the disadvantages of high smelting temperature, long smelting time, especially high tin loss ratio (>10 wt%). The tin loss attributes to the volatilization as gaseous SnO and stannous silicate ($\text{SnO}\cdot\text{SiO}_2$) residual in the slag. An innovative approach for preparing metallic tin effectively from cassiterite in the presence of Na_2CO_3 , named gas-based reduction roasting followed by water leaching process, is under development in Central South University, China. The present study, using chemically pure SnO_2 and SiO_2 , aims to determine the impact of Na_2CO_3 on the metallic tin preparation from cassiterite by the novel process using XRD, SEM-EDS, chemical analysis, etc. It was found that Na_2CO_3 effectively restrained the tin volatilization as SnO and the formation of hardly reductive $\text{SnO}\cdot\text{SiO}_2$ during the reduction roasting process. In the presence of Na_2CO_3 , most of SnO_2 in the raw materials (mixture of $\text{SnO}_2 + \text{SiO}_2$) was directly reduced to metallic tin, and part of SnO_2 reacted with Na_2CO_3 to form intermediate Na_2SnO_3 , which was then reduced to metallic tin. The SiO_2 was transformed into Na_2SiO_3 and then went into the water solution in the following water-leaching process. The main reactions of the $\text{SnO}_2 + \text{SiO}_2$ system in the presence of Na_2CO_3 under reductive atmosphere were ascertained.

Keywords: Stannic oxide; Cassiterite; Reduction roasting; Sodium carbonate; Metallic tin.

1. Introduction

Tin is one of the earliest applied metals throughout the human history. In recent decade, the global tin production and consumption amounts are in the range of 300, 000 ~ 400, 000 tons per year [1]. Traditional tin smelting processes, including air draught, reverberatory, electric and ausmelt furnaces, as reported, have the disadvantages of high smelting temperature, long smelting time, especially high tin loss ratio (>10 wt%) [2-6].

During the production for metallic tin, cassiterite concentrates must be pretreated initially by oxidizing roasting and hydrochloric acid leaching process to remove the impurities including sulfur, arsenic, antimony, iron, lead, manganese, bismuth, tungsten, etc.. However, the main gangue component, SiO_2 (about 10 wt %), is unable to be effectively wiped off [6, 7]. In the subsequent smelting process, slag-making process is required for desilicification by producing calcium silicate. Therefore, high smelting temperature and long smelting time is required for the slag-making process smoothly.

The production practice indicated that the Sn direct recovery of the existing tin smelting processes was in the range of 85 wt%~90 wt% [6, 8]. In another word, the tin loss in the smelting process was 10

wt%~15 wt%. There were two main reasons for the tin loss: 1) SnO_2 could be reduced to intermediate product SnO during the smelting process. The SnO had a larger vapor pressure at higher temperature (more than 1000 °C) [9-12], so it was volatilized into the fume and dust as the form of gaseous SnO. The percent of tin loss in the fume and dust was more than 5 wt% [6]; 2) SiO_2 in the pre-treated cassiterite concentrates would be reacted with SnO to form stannous silicate ($\text{SnO}\cdot\text{SiO}_2$). The SnO in the form of $\text{SnO}\cdot\text{SiO}_2$ had low activity coefficient, so this part of SnO was hardly reduced to metallic tin and then left in the slag [13-17]. The percent of tin loss in the slag was in the range of 1 wt% ~10 wt% [6, 8]. In the industrial production, limestone was added into the smelting furnaces because CaO was more easily combined with SiO_2 compared to SnO. Thus, part of SnO could be liberated from the hardly reductive $\text{SnO}\cdot\text{SiO}_2$. The addition of CaO, however, would further bring about the rising of the smelting temperature and increase the volatilization of gaseous SnO.

Extensive studies were carried out using solid reductive agents (graphite, coke, petroleum coke, anthracite, charcoal, coconut etc.) and gaseous reductive agents (CO , H_2 , CH_4) [9, 18-20] to reveal the reduction mechanism of SnO_2 . Nevertheless, little

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attention was paid to the reduction behaviors of SnO_2 in the presence of sodium salts. One promising but preindustrial preparation method for metallic tin was put forward by V. G. Komkov [21]. In his study, the physicochemical aspects of carbothermic reduction of cassiterite in the ionic melt were conducted using cassiterite, sodium nitrate and sodium carbonate as raw materials and low-sulfur coal as reducing agent. During the smelting process, NaNO_3 (decomposition temperature $380\text{ }^\circ\text{C}$) was decomposed into Na_2O . The new-born alkaline oxide, Na_2O , however, was detrimental to the operation life of costly refractory materials for the smelting equipments. Furthermore, the final decomposition gaseous product, NO_x , would lead to environmental pollution.

As reported in our previous study, sodium stannate (Na_2SnO_3) is prepared from chemically pure stannic oxide [22] (or cassiterite concentrates [23]) and sodium carbonate via a weak reduction roasting under CO/CO_2 atmosphere (CO content less than 30 vol %) followed by water leaching process. It was noteworthy to mention that metallic tin began to appear when the mixture of SnO_2 and Na_2CO_3 was roasted at $875\text{ }^\circ\text{C}$ for 45 min if the CO content in the mixed CO/CO_2 gas exceeded 25 vol%. In the subsequent experiments, crude tin with purity over 95% and tin direct recovery over 98% was obtained when the pretreated cassiterite and Na_2CO_3 were roasted under strong reductive atmosphere at high temperatures. Based on the findings mentioned above, a new technical route to efficiently prepare metallic tin from cassiterite and Na_2CO_3 via a reduction roasting followed by water leaching process is put forward and has been applied for a Chinese patent [24].

In order to examine the impact of Na_2CO_3 on the recovery of metallic tin from cassiterite by the novel process, chemically pure SnO_2 , SiO_2 and Na_2CO_3 were used as research objects in the present work. Effects of the roasting parameters on the tin direct recovery were firstly investigated. Then, the phase transformation, acting mechanism of Na_2CO_3 and main reactions during the reduction roasting process were further determined using XRD, SEM-EDS, chemical analysis, etc.

2. Experimental

2.1. Materials

SnO_2 , SiO_2 and Na_2CO_3 used in the study were analytical grade reagents with purity more than 99.5 wt%. As mentioned above, the percent of SiO_2 in the pretreated cassiterite concentrates before entering into the smelting furnaces was about 10 wt% [6]. Hence, 10 wt% SiO_2 was added into the SnO_2 powders served as raw materials. The tested samples were pre-ground to a particle size passing through a 200 mesh screen

(<0.074 mm). The gases used for the reduction roasting process, including CO , CO_2 and N_2 , were more than 99.99 vol% pure.

2.2. Methods

The experimental flow sheet is shown in Fig. 1. The mixture of $\text{SnO}_2 + 10\text{ wt}\% \text{SiO}_2$ and Na_2CO_3 were first mixed in a certain matching ratio. About 5.0 g mixture with 10% moisture was agglomerated to be a cylindric briquette with 10 mm in diameter and 10mm in height under the pressure of 10 MPa. The green briquettes were dried in a drying oven at $105\text{ }^\circ\text{C}$ for 4 h. Then, the experiments were carried out based on the following procedure of reduction roasting and grind-leaching.

The dried briquettes were placed into a porcelain crucible and loaded into a heat resistant quartz glass tube. The samples were then pushed to the constant temperature zone in an electrically heated horizontal tube furnace. Beforehand, the furnace was heated to a preset temperature. The roasting temperature was measured with a Pt–Rh thermocouple and controlled using a KSY Intelligent Temperature Controller (accuracy $\pm 5\text{ }^\circ\text{C}$). The experimental schematic diagram for reduction roasting is the same as that presented in the previous study [22]. Pure N_2 was introduced into the quartz tube until the temperature reached a constant value. Next, the N_2 was immediately replaced by the mixed CO/CO_2 gas. The content of CO in the CO/CO_2 mixture was adjusted by controlling the flowmeters. The inlet gas flow was fixed at $4.0\text{ dm}^3/\text{min}$. After being roasted at given temperatures for certain time, the roasted briquettes were cooled to room temperature in pure N_2 atmosphere, and then discharged from the quartz tube followed by precise weighting and grinding.

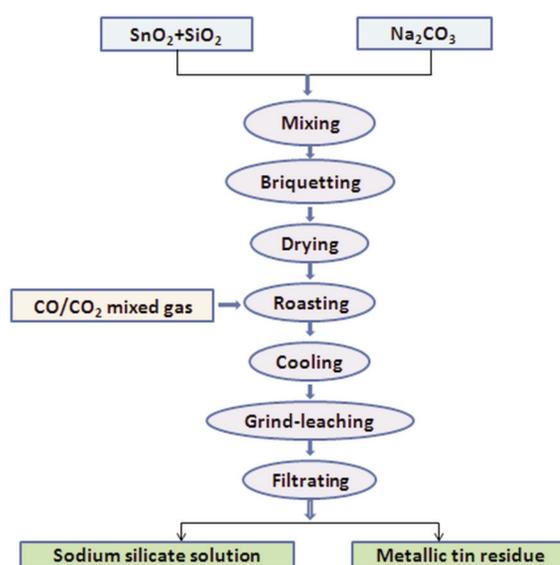


Figure 1. The experimental flowsheet

A computerized X-ray diffraction equipment (XRD, D/max 2550PC, Japan Rigaku Co., Ltd.) was used to determine phase composition of the roasted products. Some roasted products were also analyzed by the scanning electron microscope equipped with an energy diffraction spectrum (SEM-EDS, JEOL, JSM-6490LV, Japan).

After cooling, in each leaching test, 10.0 g of the roasted products was put into a ceramic ball mill for grind-leaching with hot water. Next, the leaching residue and solution were separated by filtering and prepared for the determination of metallic tin content in the residue using chemistry titration and Sn concentration in the solution using ICP-AES (ICP-AES, PS-6, American Baird Co., Ltd.).

The main phase in the leaching solution was Na_2SiO_3 as well as a small amount of Na_2SnO_3 and unreacted Na_2CO_3 . Na_2SiO_3 , Na_2CO_3 and Na_2SnO_3 were leachable easily in the water [25, 26]. According to our previous study [22], the maximum leaching efficiency of tin as the form of Na_2SnO_3 was obtained under the optimal leaching conditions: water-to-solid ratio of 4 cm^3/g , leaching temperature of 40 °C, leaching time of 45 min and stirring rate of 300 rpm. Hence, the suitable leaching conditions used in the study were chosen as the same as those mentioned above.

2.3. Evaluation indexes

2.3.1. Metallic tin content

Metallic tin content in the leaching residue is detected by way of chemical analysis. About 0.1 g sample was weighed and put into a 250 mL conical flask; 30 mL FeCl_3 solution (80 g/L) were added and vibrated for 60 min; then filtrated and washed. After that, 20 ml mixture solution of sulphuric acid and phosphoric acid (15 vol% concentrated H_2SO_4 , 15 vol% concentrated H_3PO_4 and 70 vol% deionized water) was added into the filtrate, then, potassium dichromate standard solution (2.4518 g/L is equivalent to 0.05 mol/L) was applied for the titration of the obtained solution, using sodium diphenylamin-sulfonate (5 g/L) as an indicator. The metallic tin content of the leaching residual is calculated by the following formula:

$$\theta = \frac{0.05 \times V_0}{40 \times m_0} \times 118.69 \quad (1)$$

Where θ is metallic tin content of the leaching residue, (wt %); V_0 is the potassium dichromate standard solution consumed during the titration, (mL); 118.69 is the amount of substance of Sn, (g/mol); m_0 is the actual weight of ore sample for chemical analysis, (g).

2.3.2. Sn direct recovery

The previous studies showed that the SnO

volatilizing into the flue gas [10-12] and the leachable sodium stannate [22, 23] entering into the leaching solution in the soda roasting-leaching process would lead to the loss of tin. Therefore, the Sn direct recovery was calculated in accordance with the following expressions:

$$\varepsilon = \frac{m_1 - m_2}{m_1} \times 100 \quad (2)$$

$$\gamma = \frac{1 - (1 - \varepsilon \%) \times \alpha}{\delta} \times 100 \quad (3)$$

$$\beta = \frac{C \times V}{\alpha \times m_1} \times 10^4 \quad (4)$$

$$R = 100 - \beta - \gamma \quad (5)$$

Where m_1 is the mass of the sample before reduced, (g); m_2 is the mass of the sample after reduced, (g); ε is the weight loss ratio of the sample, (wt%); γ is the tin volatilized fraction, (wt%); δ is the Sn grade of the sample before reduced, (wt%); α is the Sn grade of the roasted sample (wt%); β is the Sn loss ratio in leaching solution (wt%); C is the mass concentration of Sn in the leach liquor (g/dm^3); V is the volume of the leaching solution (dm^3); R is the Sn direct recovery (wt%).

3. Results

The effects of main parameters including Na_2CO_3 dosage, roasting temperature, CO content and roasting time on the metallic tin content and Sn direct recovery were firstly examined. Here, Na_2CO_3 dosage refers to the mass ratio of $\text{Na}_2\text{CO}_3/(\text{SnO}_2 + \text{SiO}_2)$. CO content refers to the CO volume concentration in the mixed CO-CO_2 gas (i.e., $\text{CO}/(\text{CO} + \text{CO}_2)$). After roasting, the roasted products were leached under the optimal conditions abovementioned. The different roasting conditions and corresponding results were listed in Table 1.

As observed from Table 1, the metallic tin content increased rapidly with the increase of Na_2CO_3 dosage, indicating that the presence of Na_2CO_3 was conducive to the reduction of SnO_2 . The tin volatilization fraction decreased from 1.1 wt% down to 0 wt% with Na_2CO_3 dosage increasing from 0 wt% to 30 wt%. The Sn direct recovery decreased slowly from 98.9 wt% down to 94.3 wt% when the Na_2CO_3 dosage was 10 wt%. Then, the Sn direct recovery decreased dramatically when the Na_2CO_3 dosage exceeded 10 wt% until it tended to be a constant at the Na_2CO_3 dosage of 30 wt%. Thus, Na_2CO_3 dosage of 30 wt% was recommended as the favorable value in the next experiments.

It is also shown in Table 1 that both the metallic tin content and Sn direct recovery increase markedly as the increasing of roasting temperature and time. Based on the results, 950 °C and 120 min were selected to be the suitable roasting temperature and time.

Table 1. Tin separation and direct recovery from SnO₂ + SiO₂ under different reduction conditions

Test No.	Roasting conditions				Metallic tin content in leaching residual θ / wt%	Volatilized fraction of Sn γ / wt%	Sn direct recovery R / wt%	
	Na ₂ CO ₃ dosage / wt%	Temp. / °C	CO content / vol%	Time / min				
1	0	900	50	30	40.6	1.1	98.9	
2	10				42.3	0.4	94.3	
3	20				50.2	0.2	76.1	
4	30				56	0	71.9	
5	40				64.2	0	71.7	
6	30	950	50	30	70.5	0	76.4	
7		1000			83.2		79.7	
8		950	60	30	75.2	0	69.1	
9			80		85.2		77.2	
10		950	80	90	95.2	0	93.8	
11				120	97.3		98.1	
12*		30	950	80	120	96.5	0	98.5

* Cassiterite (87.8 wt% SnO₂ and 11.0 wt% SiO₂) was set as the raw material.

The metallic tin content is enhanced from 56.0 wt% to 85.2 wt% with the increase of CO content from 50% to 80%. However, the Sn direct recovery decreases from 71.9 wt% to 69.1 wt% with increasing the CO content from 50 vol% to 60 vol%, and then increases to 77.2 wt% when the CO content further increases to 80 vol%. Hence, the CO content of 80 vol% was recommended for the subsequent experiments.

In test No. 12, cassiterite (87.8 wt% SnO₂ and 11.0 wt% SiO₂) was set as the raw material, and 96.5 wt% crude tin and 98.5 wt% Sn direct recovery were obtained under the aforementioned optimal roasting conditions.

4. Discussion on the effect of Na₂CO₃

A novel process of gas-based reduction roasting followed by water-leaching for metallic tin preparation from cassiterite in the presence of Na₂CO₃ was put forward. By this process, the Sn direct recovery was increased by 8 wt%~13 wt% compared with the traditional smelting processes in the absence of Na₂CO₃. It is concluded that Na₂CO₃ has positive impact on the recovery of tin from cassiterite. Next, the effect of Na₂CO₃ was discussed.

4.1. Phase transformation during the reduction roasting process

4.1.1. Effect of Na₂CO₃ dosage

Fig. 2 illustrates the XRD patterns of the samples roasted with diverse Na₂CO₃ dosage (Test

No. 1~5 in Table 1). It can be seen that the diffraction peaks of SiO₂ disappeared when Na₂CO₃ dosage exceeded 10 wt%, indicating that SiO₂ nearly completely reacted with Na₂CO₃ during the roasting process. From the result of test No. 2, it is inferred that a small amount of leachable Na₂SnO₃ is formed when Na₂CO₃ dosage is 10 wt%, because Na₂CO₃ was preferentially reacted with SiO₂. As the Na₂CO₃ dosage increased more than 20 wt%, there were typical diffraction peaks of Na₂SnO₃ in the XRD patterns. The diffraction peak intensity of Na₂SnO₃ enhanced with the increasing of Na₂CO₃

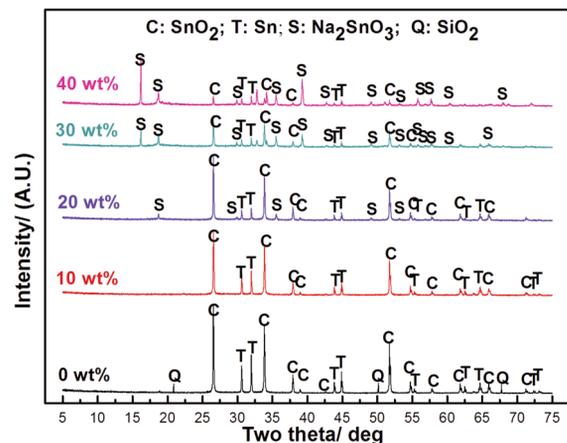


Figure 2. XRD patterns of the samples roasted at different Na₂CO₃ dosage (roasting at 900 °C for 30 min with 50 vol% CO content).

dosage. Because Na_2SnO_3 was water-soluble, so the Sn direct recovery was decreased sharply with the increase of Na_2CO_3 dosage (shown in the Table 1).

According to Table 1, the tin volatilization fraction and Sn direct recovery were 1.1 wt% and 98.9 wt% when the mixture of $\text{SnO}_2+\text{SiO}_2$ was roasted in the absence of Na_2CO_3 . However, the metallic tin content was only 40.6 wt%. This was due to the easy formation of hardly reductive $\text{SnO}\cdot\text{SiO}_2$ in the system, which is detected by SEM/EDS and shown in Fig. 3 (roasted product of test No.1 in Table 1). From Fig. 3, we can see that spot C in SEM image was $\text{SnO}\cdot\text{SiO}_2$, which was characterized by EDS analysis.

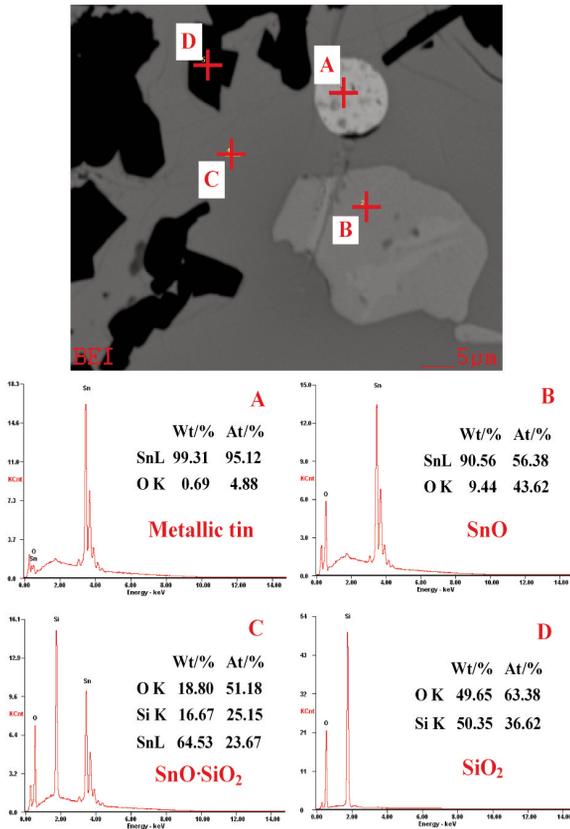


Figure 3. SEM/EDS analysis of the sample roasted in the absence of Na_2CO_3 (Test No. 1: roasting at 900 °C for 30 min with 50 vol% CO content).

4.1.2. Effect of CO content

Fig. 4 displays the XRD patterns of the samples roasted at CO content of 60 vol% and 80 vol% (Test No. 8 and 9 in Table 1). It can be seen that the diffraction peak intensity of SnO_2 and Na_2SnO_3 decreased while the diffraction peak intensity of metallic tin increased with the increase of CO content. This demonstrated that new-born Na_2SnO_3 was again reduced to metallic tin under stronger reductive atmosphere.

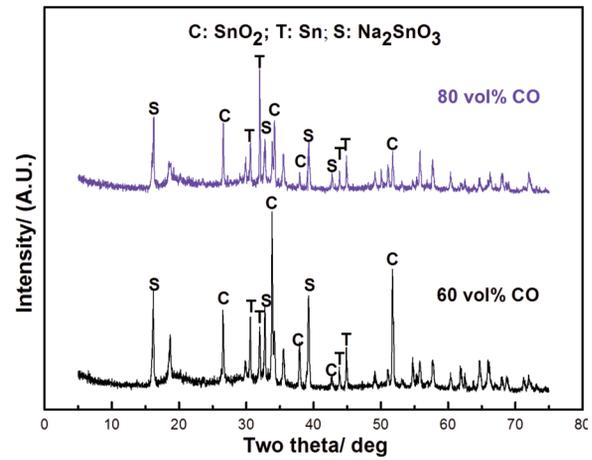


Figure 4. XRD patterns of the samples roasted at different CO contents (roasting at 950 °C for 30 min with 30 wt% Na_2CO_3 dosage).

4.2. The mechanism of Na_2CO_3 on improving the Sn direct recovery

4.2.1. Effect of Na_2CO_3 on the formation of stannous silicate

It was reported that silicate stannous was produced inevitably during the present tin smelting processes [13-17]. It was also detected by SEM/EDS and shown in Fig. 3. In order to determine the effect of Na_2CO_3 on the formation of $\text{SnO}\cdot\text{SiO}_2$, pure SnO and SiO_2 with molar ratio of 1: 1 were roasted at 950 °C for 60 min under 15 vol% CO atmosphere in the absence and presence of Na_2CO_3 , respectively. Sample 1[#] was the product roasted with SnO: SiO_2 molar ratio of 1:1 and sample 2[#] was the product roasted with SnO: SiO_2 : Na_2CO_3 molar ratio of 1:1:2.

Fig. 5 displays the XRD patterns of the sample 1[#] and 2[#]. It can be seen that a little SnO_2 and Sn were

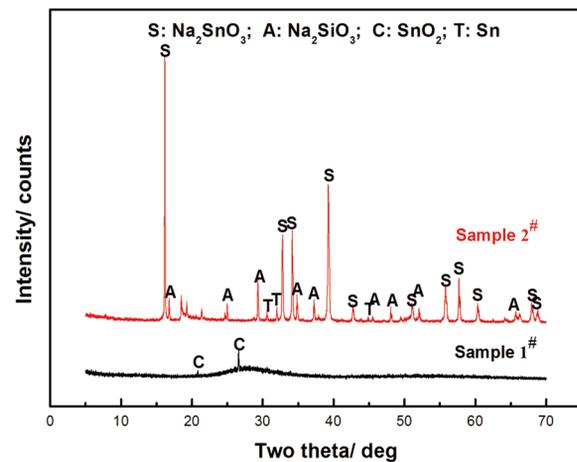


Figure 5. XRD patterns of roasted products of SnO and SiO_2 in the absence (sample 1[#]) and presence (sample 2[#]) of Na_2CO_3 (roasting temperature of 950 °C for 60 min with 15 vol% CO content).

found in the sample 1[#] and 2[#] due to the disproportion of SnO [9]; the amorphous diffraction peaks in the sample 1[#] was attributed to SnO·SiO₂, which had been identified as stannous silicate [13, 14]. The stannous silicate with low melting temperature (865 °C) [15-17] was characterized as hardly reductive tin-bearing material. However, in the sample 2[#], vast Na₂SnO₃ and Na₂SiO₃ were found when Na₂CO₃ was added into the mixture of SnO and SiO₂. It was demonstrated that the reaction of SnO and SiO₂ was changed dramatically in the presence of Na₂CO₃. Hence, the Sn direct recovery was able to be obviously improved due to the inhibition of forming hardly reductive SnO·SiO₂.

4.2.2. Effect of Na₂CO₃ on the volatilized fraction of tin

In the tin smelting process, the loss of tin in the form of SnO_(g) must be restrained as much as possible. Thus, SnO₂ and 0 ~ 40 wt% dosage Na₂CO₃ was roasted at 950 °C with 15 vol% CO content for 60 min. Here, Na₂CO₃ dosage refers to the mass ratio of Na₂CO₃ to SnO₂ (i.e., Na₂CO₃/SnO₂). Effect of Na₂CO₃ dosage on the tin volatilized fraction is determined and the results are plotted in Fig. 6.

According to Fig. 6, the tin volatilized fraction decreases from 2.0 wt% down to 0 wt% continuously with the increase of Na₂CO₃ dosage from 0 wt% up to 40 wt%. It was indicated that Na₂CO₃ restrained the volatilization of SnO. This was the other reason for the improvement of the Sn direct recovery.

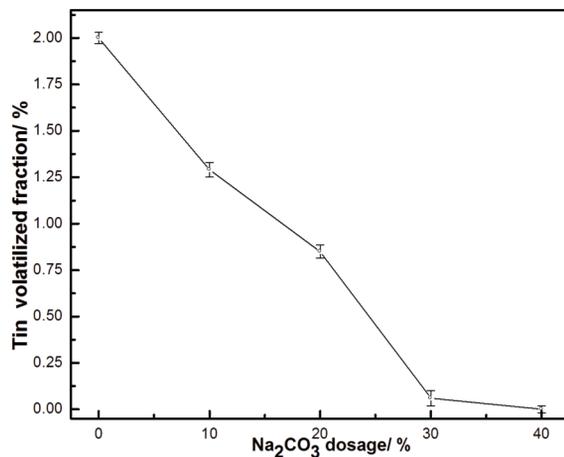


Figure 6. Effect of Na₂CO₃ dosage on the tin volatilization fraction (roasting at 950 °C for 60 min with 15 vol% CO content).

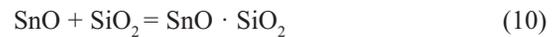
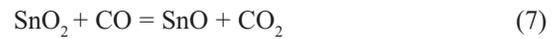
4.3. Main reactions during the reduction roasting process

The previous studies focused on the reductive reaction of tin oxides under CO/CO₂ atmosphere in

the absence of Na₂CO₃. From the analyses of Figs. 2~6, we can confirm that the main phases during the reduction roasting for SnO₂ in the presence of Na₂CO₃ were Na₂CO₃, SnO₂, Sn, SnO, SnO·SiO₂, Na₂SiO₃, Na₂SnO₃, as well as the gaseous phase CO and CO₂.

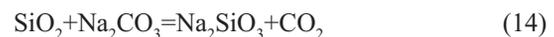
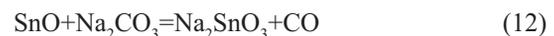
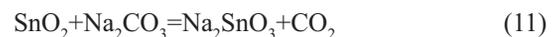
4.3.1. In the absence of Na₂CO₃

Combined with the previous researches, the main reactions during the reduction roasting for SnO₂ without Na₂CO₃ are summarized and listed as Eqs. (6)~(9). In the traditional tin smelting process, the volatilization loss of tin derived from the two reactions of Eq. (7) and (9). The formation of hardly reductive SnO·SiO₂ was ascribed to Eq. (10).



4.3.2. In the presence of Na₂CO₃

From Fig. 5, Na₂SiO₃ formed and SnO·SiO₂ disappeared when Na₂CO₃ was added into the mixture of SnO₂ and SiO₂ during the reduction process. From Fig. 6, the volatilization of SnO was restrained in the presence of Na₂CO₃. As shown in Fig. 5, SnO was able to react with Na₂CO₃ and form Na₂SnO₃. Moreover, the reduction of Na₂SnO₃ to metallic tin also existed during the reduction roasting process, which was observed from Fig. 4. Therefore, besides Eqs. (6)~(9) existing in the reduction process, some other reactions, Eqs. (11)~(15), would also take place in the presence of Na₂CO₃.



In the novel process, the restrained effect of the volatilization of SnO and formation of SnO·SiO₂ were attributed to the Eqs. (12) and Eqs. (14)~(15), respectively.

5. Conclusions

An innovative approach of reduction roasting in the presence of Na₂CO₃ followed by water-leaching process to prepare metallic tin from cassiterite has been developed by the authors' group. This study reveals the effect of Na₂CO₃ on the recovery of tin using chemically pure SnO₂ and SiO₂ as research

objects. It was found that Na_2CO_3 effectively restrained the formation of hardly reductive $\text{SnO}\cdot\text{SiO}_2$ and the volatilization of $\text{SnO}_{(g)}$. This was due to the formation of Na_2SiO_3 and intermediate Na_2SnO_3 . Then, the intermediate Na_2SnO_3 was reduced to metallic tin at higher temperature under stronger reductive atmosphere during the roasting process. Na_2SiO_3 got into the leaching solution during the following water-leaching process. As a result, the metallic tin content and Sn direct recovery of 97.3 wt% and 98.1 wt%, respectively, are achieved under the optimal experimental conditions: roasting temperature of 950 °C, CO content of 80 vol%, roasting time of 120 min and Na_2CO_3 dosage ($\text{Na}_2\text{CO}_3/(\text{SnO}_2 + \text{SiO}_2)$) of 30 wt%.

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