EFFECT OF Na₂CO₃ 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 (SnO·SiO₂) residual in the slag. An innovative approach for preparing metallic tin effectively from cassiterite in the presence of Na₂CO₃, named gas-based reduction roasting followed by water leaching process, is under development in Central South University, China. The present study, using chemically pure SnO₂ and SiO₂, aims to determine the impact of Na₂CO₃ on the metallic tin preparation from cassiterite by the novel process using XRD, SEM-EDS, chemical analysis, etc. It was found that Na₂CO₃ effectively restrained the tin volatilization as SnO and the formation of hardly reductive SnO·SiO₂ during the reduction roasting process. In the presence of Na₂CO₃, most of SnO₂ in the raw materials (mixture of SnO₂+SiO₂) was directly reduced to metallic tin, and part of SnO₂ reacted with Na₂CO₃ to form intermediate Na₂SnO₃, which was then reduced to metallic tin. The SiO₂ was transformed into Na₂SiO₃ and then went into the water solution in the following water-leaching process. The main reactions of the SnO₂ + SiO₂ system in the presence of Na₂CO₃ 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, SiO₂, (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) SnO₂ 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) SiO₂ in the pre-treated cassiterite concentrates would be reacted with SnO to form stannous silicate (SnO·SiO₂). The SnO in the form of SnO·SiO₂ 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 SiO₂ compared to SnO. Thus, part of SnO could be liberated from the hardly reductive SnO-SiO₂. 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, H₂, CH₄) [9, 18-20] to reveal the reduction mechanism of SnO₂. 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 °C) was decomposed into Na$_2$O. The new-born alkaline oxide, Na$_2$O, 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$_2$SnO$_3$) 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$_2$CO$_3$ was roasted at 875 °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$_2$CO$_3$ 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$_2$CO$_3$ 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$_2$CO$_3$ on the recovery of metallic tin from cassiterite by the novel process, chemically pure SnO$_2$, SiO$_2$ and Na$_2$CO$_3$ 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$_2$CO$_3$ 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$_2$CO$_3$ 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 SnO$_2$ + 10 wt% SiO$_2$ and Na$_2$CO$_3$ 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 10 mm in height under the pressure of 10 MPa. The green briquettes were dried in a drying oven at 105 °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 ± 5 °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 dm$^3$/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](image-url)
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 Na₂SiO₃ as well as a small amount of Na₂SnO₃ and unreacted Na₂CO₃. Na₂SiO₃, Na₂SnO₃, Na₂CO₃ and Na₂SnO₃ were leachable easily in the water [25, 26]. According to our previous study [22], the maximum leaching efficiency of tin as the form of Na₂SnO₃ was obtained under the optimal leaching conditions: water-to-solid ratio of 4 cm³/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 FeCl₃ 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 H₂SO₄, 15 vol% concentrated H₃PO₄ 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 diphenylaminedisulfonate (5 g/L) as an indicator. The metallic tin content of the leaching residual is calculated by the following formula:

$$\theta = \frac{0.05 \times V \times 118.69}{40 \times m_o}$$

Where \( \theta \) is metallic tin content of the leaching residue, (wt %); \( V \) is the potassium dichromate standard solution consumed during the titration, (mL); 118.69 is the amount of substance of Sn, (g/mol); \( m_o \) 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:

$$\epsilon = \frac{m_1 - m_2 \times 100}{m_1}$$

$$\gamma = 1-(1-\epsilon)\times \frac{\alpha \times m_1 \times 10^4}{\delta \times \gamma}$$

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

$$R = 100 - \beta - \gamma$$

Where \( m_1 \) is the mass of the sample before reduced, (g); \( m_2 \) is the mass of the sample after reduced, (g); \( \epsilon \) is the weight loss ratio of the sample, (wt%); \( \gamma \) is the tin volatilized fraction, (wt%); \( \delta \) is the Sn grade of the sample before reduced, (wt%); \( \alpha \) is the Sn grade of the roasted sample (wt%); \( \beta \) is the Sn loss ratio in leaching solution (wt%); \( C \) is the mass concentration of Sn in the leach liquor (g/dm³); \( V \) is the volume of the leaching solution (dm³); \( R \) is the Sn direct recovery (wt%).

### 3. Results

The effects of main parameters including Na₂CO₃ dosage, roasting temperature, CO content and roasting time on the metallic tin content and Sn direct recovery were firstly examined. Here, Na₂CO₃ dosage refers to the mass ratio of Na₂CO₃/(SnO₂+SiO₂). CO content refers to the CO volume concentration in the mixed CO-CO₂ gas (i.e., CO/(CO+CO₂)). 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 Na₂CO₃ dosage, indicating that the presence of Na₂CO₃ was conductive to the reduction of SnO. The tin volatilization fraction decreased from 1.1 wt% down to 0 wt% with Na₂CO₃ 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 Na₂CO₃ dosage was 10 wt%. Then, the Sn direct recovery decreased dramatically when the Na₂CO₃ dosage exceeded 10 wt% until it tended to be a constant at the Na₂CO₃ dosage of 30 wt%. Thus, Na₂CO₃ 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.
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 dosage.

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

| Test No. | Roasting conditions | Metallic tin content in leaching residual θ / wt% | Volatilized fraction of Sn γ / wt% | Sn direct recovery R / wt% |
|----------|---------------------|-----------------------------------------------|---------------------------------|--------------------------|
|          | Na₂CO₃ dosage / wt% | Temp. /°C | CO content / vol% | Time /min | 40.6 | 1.1 | 98.9 |
| 1        | 0                   | 900      | 50              | 30       | 42.3 | 0.4 | 94.3 |
| 2        | 10                  |          |                 |          | 50.2 | 0.2 | 76.1 |
| 3        | 20                  | 950      | 50              | 30       | 56   | 0   | 71.9 |
| 4        | 30                  | 950      | 60              | 30       | 64.2 | 0   | 71.7 |
| 5        | 40                  | 950      | 80              | 90       | 70.5 | 0   | 76.4 |
| 6        | 30                  | 1000     | 60              | 30       | 83.2 | 79.7 |
| 7        | 8                   | 950      | 80              | 90       | 85.2 | 77.2 |
| 8        | 10                  | 950      | 80              | 90       | 95.2 | 93.8 |
| 9        | 12                  | 120      | 80              | 120      | 97.3 | 98.1 |
| 10       | 12                  | 30       | 80              | 120      | 96.5 | 0   | 98.5 |

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

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**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% |
|----------|---------------------|-----------------------------------------------|---------------------------------|--------------------------|
|          | Na₂CO₃ dosage / wt% | Temp. /°C | CO content / vol% | Time /min | 40.6 | 1.1 | 98.9 |
| 1        | 0                   | 900      | 50              | 30       | 42.3 | 0.4 | 94.3 |
| 2        | 10                  |          |                 |          | 50.2 | 0.2 | 76.1 |
| 3        | 20                  | 950      | 50              | 30       | 56   | 0   | 71.9 |
| 4        | 30                  | 950      | 60              | 30       | 64.2 | 0   | 71.7 |
| 5        | 40                  | 950      | 80              | 90       | 70.5 | 0   | 76.4 |
| 6        | 30                  | 1000     | 60              | 30       | 83.2 | 79.7 |
| 7        | 8                   | 950      | 80              | 90       | 85.2 | 77.2 |
| 8        | 10                  | 950      | 80              | 90       | 95.2 | 93.8 |
| 9        | 12                  | 120      | 80              | 120      | 97.3 | 98.1 |
| 10       | 12                  | 30       | 80              | 120      | 96.5 | 0   | 98.5 |

* Cassiterite (87.8 wt% SnO₂ and 11.0 wt% SiO₂) was set as the raw material.
dosage. Because Na₂SnO₃ was water-soluble, so the Sn direct recovery was decreased sharply with the increase of Na₂CO₃ 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 SnO₂+SiO₂ was roasted in the absence of Na₂CO₃. However, the metallic tin content was only 40.6 wt%. This was due to the easy formation of hardly reductive SnO·SiO₂ 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 SnO-SiO₂, which was characterized by EDS analysis.

4.1.2. Effect of CO content

Fig. 4 displays the XRD patterns of the samples roasted at different CO contents (roasting at 950 °C for 30 min with 30 wt% Na₂CO₃ dosage).

4.2. The mechanism of Na₂CO₃ on improving the Sn direct recovery

4.2.1. Effect of Na₂CO₃ 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 Na₂CO₃ on the formation of SnO·SiO₂, pure SnO and SiO₂ 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 Na₂CO₃, respectively. Sample 1 was the product roasted with SnO:SiO₂ molar ratio of 1:1 and sample 2 was the product roasted with SnO:SiO₂:Na₂CO₃ 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 and Sn were
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).](image)

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).

\[
\begin{align*}
\text{SnO}₂ + 2\text{CO} &= \text{Sn} + \text{CO}₂ \\
\text{SnO}₂ + \text{CO} &= \text{SnO} + \text{CO}₂ \\
\text{SnO} + \text{CO} &= \text{Sn} + \text{CO}₂ \\
\text{SnO}₂ + \text{Sn} &= 2\text{SnO} \\
\text{SnO} + \text{SiO}₂ &= \text{SnO}·\text{SiO}₂
\end{align*}
\]

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.

\[
\begin{align*}
\text{SnO}₂ + \text{Na}₂\text{CO}₃ &= \text{Na}₂\text{SnO}₃ + \text{CO}₂ \\
\text{SnO} + \text{Na}₂\text{CO}₃ &= \text{Na}₂\text{SnO}₃ + \text{CO} \\
\text{Na}_₂\text{SnO}_₃ + 2\text{CO} &= \text{Sn} + \text{Na}₂\text{CO}_₃ + \text{CO}_₂ \\
\text{SiO}₂ + \text{Na}_₂\text{CO}₃ &= \text{Na}_₂\text{SiO}₃ + \text{CO}₂ \\
2\text{Na}_₂\text{CO}_₃ + \text{SnO}·\text{SiO}₂ &= \text{Na}_₅\text{SiO}₃ + \text{Na}_₂\text{SnO}₃ + \text{CO}
\end{align*}
\]

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 Na₂CO₃ effectively restrained the formation of hardly reductive SnO·SiO₂ and the volatilization of SnO (g). This was due to the formation of Na₂SiO₃ and intermediate Na₂SnO₃. Then, the intermediate Na₂SnO₃ was reduced to metallic tin at higher temperature under stronger reductive atmosphere during the roasting process. Na₂SiO₃ 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 Na₂CO₃ dosage (Na₂CO₃/(SnO₂ + SiO₂)) of 30 wt%.

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References

[1] U.S. Geological Survey, Mineral commodity summaries 2014, U.S. Geological Survey, 196 p.
[2] H. Louis, Metallurgy of Tin, Published by McGraw-Hill Book Company, New York, 1911.
[3] P.A. Wright, Extractive Metallurgy of Tin, 2nd Rev. ed. Elsevier Scientific Publishing Company Press, New York, 1982.
[4] R. Smith, The Bulletin of the Peak District Mines Historical Society, 13 (1996) 91-99.
[5] X.C. Song, China Nonferrous Metallurgy, 6 (2005), 33-36. (in Chinese)
[6] X.-C. Song, Tin Metallurgy, Metallurgical Industry Press, Beijing, 2011. (in Chinese)
[7] J.S.J. Van Deventer, Thermochimica Acta, 124 (1988) 109-118.
[8] W.-S. Huang, Stannum, Metallurgical Industry Press, Beijing, 2000. (in Chinese)
[9] J. C. Platteeuw, G. Meyer, Transaction of Faraday Society, 52 (1956) 1066-1073.
[10] Y.B. Zhang, T. Jiang, G.H. Li, Z.C. Huang, Y.F. Guo, Ironmak. Steelmak., 38 (2011) 613–619.
[11] Y.B. Zhang, T. Jiang, G.H. Li, Y.F. Guo, Z.C. Huang, Int. J. Miner. Process., 110-111 (2012) 109-116.
[12] Y.B. Zhang, Z.J. Su, Y.L. Zhou, G.H. Li, T. Jiang, Int. J. Miner. Process., 124 (2013) 15-19.
[13] R.Z. Deng, Q.W. Luo, G.M. Feng, X.L. Li, Nonferrous Metals (Extractive Metallurgy), 2 (1991) 36-39. (in Chinese)
[14] R.Z. Deng, G.M. Feng, Q.W. Luo, X.L. Li, Non-ferrous Mining and Metallurgy, 3 (1991) 37-41. (in Chinese)
[15] F. He, Z.J. Li, Chemical Metallurgy, 4 (1985) 63-66. (in Chinese)
[16] Z.J. Li, A.C. Lu, E.T. Sun, Acta Metallurgica Sinica, 7 (1964) 383-390. (in Chinese)
[17] Z.J. Li, Journal of Kunming University of Science and Technology (Natural Science Edition), 4 (1979) 1-7. (in Chinese)
[18] S. Cetinkaya, S. Eroglu, Int. J. Miner. Process. 110–111 (2012) 71–73.
[19] B.S. Kim, J.C. Lee, H.S. Yoon, S.K. Kim, Materials Transactions, 9 (2011) 1814-1817.
[20] R. Padilla, H.Y. Sohn, Metallurgical Transaction B 10B (1979) 109-115.
[21] V.G. Komkova, V. V. Gostishchev, E. Kh. Ri, Russian Journal of Non-Ferrous Metals, 50 (2009) 596–599.
[22] Y.B. Zhang, Z.J. Su, B.B. Liu, Z.X. You, G. Yang, G.H. Li, T. Jiang, Hydrometallurgy, 146 (2014) 82–88.
[23] Y.B. Zhang, Z.J. Su, Z.X. You, B.B. Liu, G. Yang, G.H. Li, T. Jiang, Rare Metal Technology, Conference Proceeding, TMS 2014, 163-169.
[24] Y.B. Zhang, T. Jiang , G.H. Li, B.B. Liu, Chinese Patent 201410347188.7.
[25] A.L. Chen, Z.W. Zhao, D. Xu, X.-H. Liu, X.-Y. Chen, Hydrometallurgy, 136 (2013) 46-50.
[26] M.S. Khan, S.N. Rogak, J. Supercrit. Fluid., 30 (2004) 359-373.