Original Article

New understanding on the separation of tin from magnetite-type, tin-bearing tailings via mineral phase reconstruction processes

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A B S T R A C T

Magnetite-type tin-bearing tailing is a typically complex secondary resource in China, of which iron and tin are with greater value. The utilization of this resource has long been a challenge due to the complex mineralogy of tin and iron minerals. In this study, the mineralogical characteristics of the tailings were studied. It was found that tin mainly existed as fine-grained cassiterite and lattice Sn$^{4+}$ (Fe$_3$Sn$_3$O$_4$) in magnetite particles, which was almost impossible to recover by physical mineral processing. Fe$_{2.6}$Sn$_{0.4}$O$_4$ samples were synthesized to study the mineral phase reconstructions of Fe$_3$Sn$_3$O$_4$ under CO–CO$_2$ atmosphere, as well as in the presence of Na$_2$CO$_3$ or CaO. Then, three proposed processes of selective reduction roasting, sodium roasting and calcium roasting processes were demonstrated and applied in the separation of tin and iron. Finally, some suggestions were recommended for the separation of tin from magnetite-type tin-bearing tailings.

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1. Introduction

Tin is an important component and widely applied in electrical and electronic equipment (EEE) [1,2]. Since the third revolution of science and technology, global tin consumption demand increases annually, however, the tin reserves reduce rapidly and will be exhaust in 20 years [1]. Hence, more attention have been paid on the recovery of tin from secondary resources, such as tailings, slags, waste EEEs, etc [3].

Tin-bearing skarn iron ore is considered as one of the most complex iron ore resources in China [4,5]. Cassiterite is the only economic tin-bearing mineral from which tin metal is extracted [6]. Due to the compact embedding and fine-grained distribution of cassiterite in iron-bearing minerals and gangue minerals, it’s difficult to recover tin from the Fe-Sn skarn iron ores using the present physical mineral processing methods, including gravity, magnetic and flotation [7]. On the other hand, the residual tin content remained in the iron concentrates is always more than 0.08 wt.%, which can’t be used as

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iron-making burdens [8]. Hence, little attention has been paid to the recovery of iron-bearing minerals from the complex resources, so they were discharged as tailings during traditional cassiterite mineral processing.

The reserves of high-grade tin resources were almost exhausted in recent years, especially in China, the economic cutoff tin grade for the mineral processing was decreased from 0.56 wt.% to 0.25 wt.% during the past 20 years [9]. Therefore, tin-bearing tailings become an important secondary resource for tin recycling [1–3]. Based on the type of iron-bearing minerals, two kinds of tin-, iron-bearing tailings were classified, which included magnetite type and hematite-limonite type. The phase composition of iron was subject to the mineralizing conditions, especially the redox state of the hydrothermal fluid [6,7]. Hence, the forms of tin-bearing minerals were different associated with two types of iron-bearing minerals.

Some researchers on mineralogy and geochemistry have classified that part of tin in the tailings as non-cassiterite phases [10]. Especially in tin-bearing skarn, tin was found as exsolution colloidal grains, malayaite, stokesite, stannite, etc [11–14]. During the geological mineralization process, the formation stage of cassiterite and magnetite were coincident for similar temperature and oxidation-reduction state of the magmatic hydrothermal fluid [14]. Then the replacement of octahedron coordinated Fe³⁺ by the 6 coordinated Sn⁴⁺ in magnetite occurred and Sn⁴⁺ was disperse distributed in the lattice of magnetite, while the lattice Sn⁴⁺ was common in tin-bearing magnetite (Fe₂Sn₃O₄) and the distribution ratio was in the range of 20–70 wt.% Therefore, this kind of tin can’t be separated and recovered only by mineral processing, and tin was remained in the magnetite concentrate. Fuming processes, such as sulfurization and chlorination roasting, are practised to separate tin from middle-grade tin-bearing materials of tin-ore tailings and tin smelting slag [8]. But the iron oxides would be reduced to FeO which was impossible to recover, moreover, fuming processes were not economically feasible for the high roasting temperature and low grade of tin of raw materials. In addition, the reduction and volatilization behavior of Fe₂Sn₃O₄ phase were unclear.

Our previous studies have indicated SnO₂ was much easier to react with CaO or Na₂CO₃ under CO–CO₂ atmosphere [15,16]. Above theoretical basis was taken into practice to separate tin and iron from cassiterite-hematite type tailings. The formation of calcium stannates were confirmed to promote during the magnetizing roasting process, then the mineral phase of tailings were reconstructed, which was benefit for the separation and recovery of tin [17]. A magnetic concentrate containing 66.3 wt.% total iron and 0.07 wt.% tin was obtained from this type of tailings, which could be used as high-quality burdens for preparing direct reduced iron.

Hence, in this study, research on mineral phase reconstruction of magnetite-type tin-bearing was taken into consideration, while synthetic Fe₂Sn₃O₄ was used as raw material to investigate the law and characteristics of phase transformation. Reduction behaviors of Fe₂Sn₃O₄ reactions between Fe₂Sn₃O₄-CaO as well as Fe₂Sn₃O₄-Na₂CO₃ were also studied. In addition, proposed processes for the separation of tin from magnetic-type tin-bearing tailings were put forward and investigated.

2. Experimental

2.1. Materials

2.1.1. Magnetite-type tin-bearing tailings

The magnetite-type tin-bearing tailings were taken from Yunnan province, China. The major chemical compositions given in Table 1 were determined by XRF (X-ray Fluorescence, Axios mAX) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry, IRIS Intrepid II XSP). It can be seen from Table 1 that the total iron and tin content in the tailings were as high as 38.83 wt.% and 0.358 wt.%, and the main impurities compositions were 10.46 wt.% CaO, 18.85 wt.% SiO₂, 4.30 wt.% Al₂O₃ and 2.01 wt.% MgO. The sieve analysis results indicated that the granularity of the tailings below 0.075 mm and 0.045 mm were found as 78.26 wt.% and 52.24 wt.% respectively.

The XRD (X-Ray Powder Diffraction, D/max 2550PC, Japan Rigaku Co., Ltd) pattern of the tailings is shown in Fig. 1-a, which indicated that iron existed in the forms of magnetite and garnets (mainly andradite (Ca₃Fe₂(SiO₄)₃) and grossularite (Ca₃Al₂(SiO₄)₃)), and quartz was the main gangue mineral. However, garnets (andradite and grossularite) were the main Ca-bearing minerals.

The microstructure of the tailing sample is observed by SEM-EDS (FEI QUANTA 200; FEI, Eindhoven, equipped with an EDAX energy dispersive x-ray spectroscopy (EDS)), and the results are shown in Fig. 1-b. In Fig. 1-b, cassiterite was found as individual particle and closely embedded in magnetite or garnet. The particle size of cassiterite was mainly within 5 μm, and it was almost impossible to recover the cassiterite by flotation or gravity separation [7]. Meanwhile, parts of magnetite disseminated in andradite and grossularite, which probably decreased the grade and recovery of iron during the magnetic separating process [8].

In order to further investigate the occurrence state of iron and tin in the magnetite, electron microprobe analysis (EMPA, NanoManVS + Multimode) was conducted and the results are presented in Fig. 1-c. The results in Fig. 1-c indicated that no independent cassiterite existed in the particle of magnetite, and the EMPA compositions of Spot D–G showed that the tin content was in the range of 0.21–0.29 wt.%. The EMPA mapping of Sn (in Fig. 1-d) further revealed that tin was dispersed distribution in the lattice of magnetite, and no cassiterite was found. Based on previous studies of geochemistry, this kind of tin was the lattice Sn⁴⁺, which substituted Fe³⁺ in the magnetite lattice [14].

The tin content in the tailings was too low to determine the phase compositions by XRD, SEM and EMPA, hence, chemical phase analysis was used to investigate the phase of tin in the tailings in this study [11–14]. Previous studies declared that cassiterite was insoluble when it was treated with 1:3 sulfuric acid, and the acid-soluble tin was always used to determine the non-cassiterite phase [18]. The results in Table 2 showed that the content of tin in cassiterite was 0.245 wt.%, while the acid-soluble tin content was as high as 0.113 wt.% with a distribution ratio of 31.56 wt.%.

The results in Fig. 1 and Table 2 indicated that two types of tin-bearing phases were existed in the tailings, fine cassi-
Table 1 – Main chemical compositions of magnetite-type tin-bearing tailings.

<table>
<thead>
<tr>
<th>Components</th>
<th>TFe</th>
<th>Sn</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>TiO₂</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt.%)</td>
<td>38.82</td>
<td>0.358</td>
<td>10.46</td>
<td>18.85</td>
<td>4.30</td>
<td>2.01</td>
<td>0.40</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Fig. 1 – The process mineralogy analysis of magnetite-type tin-bearing tailings (a-XRD pattern; b- SEM image; c, d, e and f-EPMA images).

terite compactly embedded in magnetite and lattice Sn⁴⁺ in magnetite.

2.1.2. Synthetic Fe₃₋ₓSnₓO₄ samples
Fe₃₋ₓSnₓO₄ (x = 0.4) was prepared from SnO₂, Fe₂O₃ and metallic iron (AR reagents with a purity of more than 99.8 wt.%) based on previous researches [19], and the synthetic Fe₃₋ₓSnₓO₄ were ground to 100% particle size less than 0.074 mm. The XRD pattern of the synthetic Fe₃₋ₓSnₓO₄ is shown in Fig. 2. The results indicated that the product was with a high purity and well matched with the PDF standard card (PDF# 71-0694) and no diffraction peaks of impurities were found.

2.2. Methods

All the roasting tests were conducted in a horizontal controlled atmosphere resistance furnace as our previous studies [17,20]. The samples were first mixed with a certain amount of CaO/Na₂CO₃ and then placed in a corundum porcelain boat and send into the roasting area of the furnace. The N₂ gas was first inlet to displace the air in the quartz reactor. After the temperature achieved the setting value, CO–CO₂ mixed
gas replaced N₂ gas and reactions were conducted. The total flow rate of the CO–CO₂ mixed gas was fixed at 4.0 L/min, and the CO content refers to the CO volume concentration in the CO–CO₂ mixed gas (i.e., CO/(CO + CO₂)). After roasting at given temperatures for a period, the samples were rapidly taken out and quenched into liquid nitrogen to prevent the oxidation of the roasted products.

Wet-grinding and magnetic separation tests were conducted in a ball mill (XMQ#240°90, grinding concentration of 50 wt.%) and a magnetic separator (Model: XCGS-73, Davis magnetic tube, magnetic field intensity of 0.10T).

### 3. Results and discussion

#### 3.1. Mineral phase reconstructions of Fe₃ₓSn₄O₄

Plenty of our studies have researched the reduction behavior of SnO₂, as well as the reactions of SnO₂-Na₂CO₃ and SnO₂-CaO [8,16,20]. As observed in Section 2.1, Fe₃ₓSn₄O₄ was a complex phase in tailings, which have been paid little attention. In this section, synthetic Fe₃ₓSn₄O₄ samples were used as raw materials. Reduction behavior of Fe₃ₓSn₄O₄, and reactions between Fe₃ₓSn₄O₄-CaO as well as Fe₃ₓSn₄O₄-Na₂CO₃ were investigated, respectively.

##### 3.1.1. Reduction of Fe₃ₓSn₄O₄ under CO–CO₂ atmosphere

Our previous researches indicated that Fe₂O₃ and SnO₂ were synchronously reduced stepwise according to Fe₂O₃→Fe₂O→Fe and SnO₂→SnO→Sn, and the gas-phase equilibrium diagram of FeOx and SnOx under CO–CO₂ atmosphere was calculated and plotted in Fig. 3 [8,21,22]. Stable coexistence zone of Fe₂O₄-SnO₄(g) and FeO-SnO₂(g) were found in Fig. 3. However, a gas-solid reaction between Fe₂O₄ and SnO₂(g) was revealed, which was not beneficial to the volatilization and separation of SnO₂(g) [23,24].

Then the most probable thermodynamic condition for Sn volatilization should be controlled accurately in the shadow region (in Fig. 3), where FeO and SnO₂(g) were steady existence at a higher temperature.

Based on the thermomechanical analysis, exploring tests were conducted by using synthetic Fe₃ₓSn₄O₄ as raw materials under different CO–CO₂ atmosphere at 1000 °C with roasting time 60 min, and the XRD patterns of the roasted products are shown in Fig. 4. It was observed in Fig. 4 that only diffraction peaks of Fe₃ₓSn₄O₄ were found when the CO content was 10 vol.% and 20 vol.%, indicating that the Fe₃ₓSn₄O₄ spinel structure was unchanged and SnO could not be volatilized. As the CO content increased to 30 vol.% and 50 vol.%, FeO was formed and no diffraction peaks of SnO were found in the roasted products. Hence, tin was possible to volatilize under such conditions, which could be expressed as Eq. (1). However, as CO content increased to 70 vol.%, SnO was easily reduced to metallic tin in the products, as Eq. (2), which would inhibit the separation of tin from iron oxides.

\[
\text{Fe}_3x\text{Sn}_4\text{O}_4 + \text{CO}_2 = (3-x)\text{FeO} + x\text{SnO}_2(g) + x\text{CO}\quad (1)
\]

\[
\text{Fe}_3x\text{Sn}_4\text{O}_4 + (1+x)\text{CO}_2 = 3\text{FeO} + (1+x)\text{CO}_2(g) + x\text{Sn}\quad (2)
\]

The results in Fig. 3 and Fig. 4 revealed that Fe₃ₓSn₄O₄ was possibly reduced under CO–CO₂ atmosphere, so the thermodynamic condition should be controlled in the stable coexistence zone of FeO and SnO₂(g) in order to separate tin from Fe₃ₓSn₄O₄.

##### 3.1.2. Reaction between Fe₃ₓSn₄O₄ and Na₂CO₃

Sodium salt was a common additive widely used during the mineral phase reconstruction processes [25–27], and our previous studies have verified the acceleration of CO–CO₂ atmosphere on the reaction between Na₂CO₃ and SnO₂ as Eq (3) [15,20].

\[
\text{SnO}_2 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{SnO}_3 + \text{CO}_2(g) \quad (3)
\]

The reactions between Fe₃ₓSn₄O₄ and Na₂CO₃ were investigated in this section, synthetic Fe₃₋ₓSn₀₋ₓO₄ was first mixed
with Na$_2$CO$_3$ (AR reagent) as Na/Sn mole ratio of 2/1, then roasted under 10 vol.% CO content for 60 min at 600–1000 °C. Fig. 5 illustrates the effect of roasting temperature on the phase transformation of Fe$_{3-x}$Sn$_x$O$_4$. The results in Fig. 5 demonstrated that phase constituents of the roasted products were unchanged as Fe$_{3-x}$Sn$_x$O$_4$ and Na$_2$CO$_3$ at 600 °C. However, Na$_2$SnO$_3$ was formed as the roasting temperature increased to 700 °C, and the diffraction peaks of Na$_2$SnO$_3$ enhanced obviously as the roasting temperature further increased up to 1000 °C. Meanwhile, it was found by careful observation that Fe$_{3-x}$Sn$_x$O$_4$ was converted gradually into Fe$_3$O$_4$ from 700 to 1000 °C, which inferred that higher roasting temperature promoted the reaction between Na$_2$CO$_3$ and Fe$_{3-x}$Sn$_x$O$_4$, as Eq. (4). Based on our previous studies, Na$_2$SnO$_3$ was soluble in low concentration NaOH solutions, and a sodium roasting process was put forward for the separation of tin from Fe$_{3-x}$Sn$_x$O$_4$.

\[
\text{Fe}_{3-x}\text{Sn}_x\text{O}_4 + x\text{Na}_2\text{CO}_3 = (3-x)/3\text{Fe}_3\text{O}_4 + x\text{Na}_2\text{SnO}_3 + (2x/3)\text{CO} + (x/3)\text{CO}_2 (4)
\]

3.1.3. Reaction between Fe$_{3-x}$Sn$_x$O$_4$ and CaO
During a mineral phase reconstruction followed by magnetic separation process, the formation of calcium stannates from CaO and SnO$_2$ (Eq.(5)) have proved to promote the separation of tin from cassiterite-hematite type tailings [17].

\[
\text{CaO + SnO}_2 = \text{CaSnO}_3 (5)
\]

Then the reactions between Fe$_{3-x}$Sn$_x$O$_4$ and CaO were taken into consideration. Mixed sample of Fe$_{2.6}$Sn$_{0.4}$O$_4$ and CaO (AR reagent) (Ca/Sn mole ratio of 1/1) were roasted under 10 vol.% CO content for 60 min, and the effect of roasting temperature on the phase evolution of Fe$_{2.6}$Sn$_{0.4}$O$_4$ was investigated. The XRD patterns of the roasted products are shown in Fig. 6. It was observed from Fig. 6 that CaO had much stronger affinity to tin oxides than FeOx. The reactions between CaO and Fe$_{3-x}$Sn$_x$O$_4$ started when roasting temperature was higher than 800 °C, and higher roasting temperature promoted the reaction as expressed in Eq. (6). It was found by careful observation that Fe$_{2.6}$Sn$_{0.4}$O$_4$ was converted gradually into Fe$_3$O$_4$ in the characteristic peak of (311), and the diffraction peaks of CaSnO$_3$ were enhanced obviously as the roasting temperature increased to higher than 800 °C. Calcium stannates were non-magnetic materials and Fe$_3$O$_4$ was ferromagnetic, then tin-bearing compounds could be separated from iron oxides during a magnetic separation process. However, Ca$_2$Fe$_2$O$_5$ was found in the roasted products when roasting temperature was higher than 900 °C, which was adverse to the separation of iron and tin [28].

\[
\text{Fe}_{3-x}\text{Sn}_x\text{O}_4 + x\text{CaO} + (2x/3)\text{CO}_2 = (3-x)/3\text{Fe}_3\text{O}_4 + x\text{CaSnO}_3 + (2x/3)\text{CO} (6)
\]

3.2. Proposed processes for the separation of tin from magnetite-type tin-bearing tailings

Based on the results in Section 3.1, three proposed processes for the separation of tin and iron were put forward (in Fig. 7), and probe trials were demonstrated using magnetite type tin-bearing tailings as raw materials. In addition, desired mineral phase reconstructions of tin-bearing minerals were also presented in Fig. 7.

3.2.1. Selective reduction roasting process
Our previous researches have indicated that both of Ca and Si-bearing minerals have adverse effect on volatilization of SnO$_2$ [23,24], and a magnetic separation experiment followed by a selective reduction roasting process was conducted as the flowsheet shown in Fig. 7-a. A tin-bearing iron concentrate with an iron content of 64.36 wt.% was obtained first, while the tin content was as high as 0.253 wt.%. Then the effect of
roasting parameters on the separation of tin was investigated, and the results were shown in Fig. 8 and Table 3.

As presented in Fig. 8-a, the Sn content in the roasted products decreased first and then increased with the CO content increasing from 10 vol.% to 70 vol.% It was found that the optimal CO content was 30 vol.% The result was in accordance with the theoretical analysis in Section 3.1.1. The desired mineral phase of tin-bearing mineral was FeO and SnO\(_2\). It can be observed from Fig. 8-a and Fig. 8-b that higher roasting temperature and CO content led to the over reduction of tin oxides, which decreased the Sn volatilization. Under the optimal roasting conditions (roasting temperature of 975 °C, CO content of 30 vol.%, roasting time of 60 min), the tin content in the roasted product was decreased to 0.061 wt.% while tin was enriched in the volatilization dusts.

The XRD analysis and SEM-EDS image of the roasted product under the optimal roasting conditions are demonstrated in Fig. 9. It was observed from Fig. 9-a that FeO was the only phase in the roasted products, and there was no diffraction peak of impurities. The EDS results presented in Fig. 9-b indicated that Fe-O and Fe-Si-O compounds existed in the products, the mole ratio of elements were approach to 1:1 (Fe:O) and 2:1:4 (Fe:Si:O), which illustrated that FeO and Fe\(_2\)SiO\(_4\) were formed during the reduction roasting process. However, Fe\(_2\)SiO\(_4\) was amorphous phase and could not be determined by XRD analysis (in Fig. 9-a).

3.2.2. Sodium roasting followed by a magnetic separation process

The results in Section 3.1.2 and our previous studies indicated that both of SnO\(_2\) and Fe\(_{3-x}\)Sn\(_x\)O\(_4\) were easily reacted with Na\(_2\)CO\(_3\). Na\(_2\)SnO\(_3\) was formed and the compact structures of tin and iron-bearing minerals were easily destroyed. Hence, a sodium roasting followed by a magnetic separation process was proposed as Fig. 7-b. The effect of roasting parameters
Fig. 7 – Schematic diagram for the separation of tin from iron, tin-bearing tailings.
on the separation of tin and iron were investigated. The tin content in the magnetic materials was determined, and the results are shown in Fig. 10 and Table 3.

As shown in Fig. 10, Na$_2$CO$_3$ dosage and roasting temperature have the most significant effect on the separation of tin. Tin content in the magnetic products was almost unchanged when no Na$_2$CO$_3$ was used in Fig. 10-a, and the value decreased obviously as the increase of Na$_2$CO$_3$ dosage. Higher Na$_2$CO$_3$ dosage would promote the reactions between gangue components and Na$_2$CO$_3$, which led to the formation of low melting point materials (Na$_2$SiO$_3$, etc) and was not good for the separation of tin. The results in Fig. 10-c revealed that higher roasting temperature enhanced the separation of tin, which was in accord with the analysis in Fig. 4 and Eq. (4). Based on the results of Fig. 10, the optimal roasting parameters were obtained as follows: Na$_2$CO$_3$ dosage of 5 wt.%, roasting temperature of 1000 °C, CO content of 10 vol.% and roasting time of 90 min. A magnetic concentrate containing 0.113 wt.% total Sn and 62.83 wt.% total Fe was obtained, which could be used as ironmaking materials for blast furnace. However, it was found that the tin content was only 0.301 wt.% in the non-magnetic material, and part of tin was dissolved into water during the wet-grinding and magnetic separation process.

3.2.3. Calcium roasting followed by a magnetic separation process
CaO was proved to be beneficial for the separation of tin and iron from cassiterite-hematite type tailings [17], and CaO could promote the dissociation of the lattice Sn from magnetite as Eq (6). Then, in this section, CaO was used as an additive. The effect of roasting parameters on the separation of tin from the magnetite-type tailings were investigated and presented in Fig. 11 and Table 4.

As shown in Fig. 11-a, the tin content in the magnetic material decreased obviously from 0.231 wt.% to 0.121 wt.%, as the CaO dosage increased from 0 wt.% to 10.0 wt.. While the tin content was almost unchanged as the CaO dosage further increased. The results in Fig. 11-b demonstrated that the tin content in the magnetic materials decreased from 0.223 wt.% to 0.119 wt.% as the roasting temperature increased.
Fig. 10 – Effect of roasting parameters on the separation of tin during the sodium roasting followed by a magnetic separation process (tin content in magnetic materials).

Fig. 11 – Effect of roasting parameters on the separation of tin during the calcium roasting followed by a magnetic separation process (tin content in magnetic materials).

Table 4 – Results obtained under the optimal conditions (CaO dosage of 5 wt.%, roasting temperature of 825 °C, CO content of 10 vol.%, roasting time of 120 min).

<table>
<thead>
<tr>
<th></th>
<th>Yield/wt.%</th>
<th>Grade/wt.%</th>
<th>Recovery/wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Sn</td>
<td>Fe</td>
</tr>
<tr>
<td>Roasted products</td>
<td>–</td>
<td>36.49</td>
<td>0.336</td>
</tr>
<tr>
<td>Magnetite material</td>
<td>51.6</td>
<td>63.50</td>
<td>0.091</td>
</tr>
<tr>
<td>Non-magnetite material</td>
<td>54.3</td>
<td>6.86</td>
<td>0.526</td>
</tr>
</tbody>
</table>
from 700 °C to 825 °C, and the tin content increased slightly when the roasting temperature increased further. Fig. 11-d revealed the tin content decreased as the increase of roasting time. The minimum value of tin content in the magnetic material was 0.091 wt.% when the roasting time was 120 min.

Based on the results in Fig. 11, the optimal roasting parameters were obtained as follows: CaO dosage of 10 wt.%, roasting temperature of 825 °C, CO content of 5 vol.%) and roasting time of 120 min. A magnetic concentrate containing 0.091 wt.% TSn was obtained, and the tin content in the non-magnetic material was enriched to 0.526 wt.%.

In order to further determine the phase transformation of the tin-bearing tailings during the calcined roasting process, SEM-EDS and EMPA analyses of the roasted products obtained under the optimal parameters were presented in Fig. 12. In Fig. 12-a, Ca-Sn-O compounds (Spot A and B in) were found in the outer layer of the Ca-bearing compounds. The results indicated that CaO additives could react with the tin compounds (SnO₂ and Fe₂₋₃SnₓO₄₋₃) as Eq.(5) and Eq.(6), which obviously promoted the separation of tin and iron during the following magnetic separation process. The EPMA analysis of the magnetic material shown in Fig. 12-1-b indicated that the tin content in the magnetite decreased obviously to 0.084 wt.% compared with the raw material (in Fig. 1). However, the solid state reaction of Eq.(6) was likely to be restricted by the ionic migration of Sn⁴⁺ [19]. In addition, a few ultrafine cassiterite grained below 2 μm was found closely embedded in magnetite, while the mineral phase reconstructions were limited and those tin was remained in the magnetic materials.

3.3. Discussion on utilization of magnetite-type tin-bearing tailings

The mineralogical characteristics of the magnetite-type tin-bearing tailings indicated that tin mainly existed as fine particles cassiterite (SnO₂) and lattice Sn⁴⁺ (Fe₂₋₃SnₓO₄₋₃) in the magnetite. In order to utilize the tailing, both types of tin minerals should be taken into consideration. Then, three processes of selective reduction, sodium roasting and calcium roasting were proposed based on the mineral phase reconstructions of Fe₂₋₃SnₓO₄₋₃.

Both types of tin in SnO₂ and Fe₂₋₃SnₓO₄ could volatilize efficiently during selective reduction process, the suitable CO content and temperature region should be controlled strictly as the coexistence region of FeO and SnO (in Fig. 3). However, both of iron and tin oxides were easily reacted with gangues (silicon and calcium oxides) under reduction volatilization conditions, which decreased the tin volatilization. Besides, FeO and olivine (Fe₉Si₅O₁₄, CaFe₆Si₂O₁₄, etc) was impossible to recover from the roasted products [29]. Hence, a magnetic separation followed by selective reduction roasting process as Fig. 7-a was much rational, iron concentrates was first separated from the gangues, and then high quality FeO pellet and Sn-bearing dusts were obtained.

The chemical reactivity of Na₂CO₃ was much stronger, and Na₃SnO₃ was easily formed from SnO₂-Na₂CO₃ and Fe₂₋₃SnₓO₄-Na₂CO₃. But sodium salts and sodium-bearing compounds had low melting point (such as sodium silicates and sodium aluminates), which was adverse to the separation of tin from iron-bearing minerals. In addition, Na₃SnO₃ was soluble under weakly alkaline condition, which increased the difficulty of tin recovery. About 51.5 wt.% of Sn was lost in the pulp during the wet-grinding and magnetic separation process as shown in Table 3. In a word, sodium roasting was not a suitable process for the separation and recovery of tin from tailings.

CaO could promote the mineral phase reconstructions of tin-bearing minerals (SnO and Fe₂₋₃SnₓO₄₋₃ at low roasting temperature. At roasting temperature of 800-850 °C, the reactions between CaO and SnO₂ (or Fe₂₋₃SnₓO₄₋₃) were strengthened and calcium stannates were obtained, while the reactions between CaO and iron oxides were restricted. Calcium stannates had much stable chemical property, which were kept unchanged during the grinding and magnetic separation process. Then tin-bearing minerals could be separated from the iron-bearing minerals and enriched in the non-magnetic materials. In addition, high quality iron concentrates with a relatively low tin content was recovered, which can be used as blast furnace (BF) raw materials.

4. Conclusions

(1) The mineralogical characters results of the magnetite-skarn tin-bearing tailings indicated that tin was mainly existed as fine particles cassiterite and lattice Sn⁴⁺.
2. Three mineral phase reconstruction schemes of Fe₃₋ₓSnₓO₄ were investigated. Fe₃₋ₓSnₓO₄ can be reduced to FeO and SnO₂ as \( \text{Fe}_3+x\text{Sn}_x\text{O}_4 + \text{CO} = (3-X)\text{FeO} + \text{CO}_2 + X\text{SnO}_2 \) under suitable CO–CO₂ atmosphere. Optimal CO content should be controlled as 30–50 vol.%, otherwise metallic tin would be formed restricting the volatilization of tin. The reactions between Fe₃₋ₓSnₓO₄ and Na₂CO₃ (or CaO) also happened as Fe₃₋ₓSnₓO₄ + XNa₂CO₃ = \( (3-X)/3\text{Fe}_3\text{O}_4 + X\text{Na}_2\text{SnO}_3 \) + \( (2X/3)\text{CO} \). The formation of Na₂SnO₃ and CaSnO₂ destroyed the closely embedded relationship of iron and tin-bearing minerals, which promoted the separation of tin from Fe₃₋ₓSnₓO₄.

3. Three proposed processes for the separation of tin and iron from tailings were put forward based on the mineral phase reconstruction of Fe₃₋ₓSnₓO₄. Selective reduction roasting process was able to separate tin efficiently from tin-bearing minerals (SnO₂ and Fe₃₋ₓSnₓO₄), and desired mineral phase was FeO and SnO₂. Calcium stannate seemed like a perfect reconstruction phase, which could be generated at a relatively low temperature of 800–850 °C and remain stable during the following physical mineral process. Finally, a magnetic concentrate containing 0.091 wt.% total tin was obtained and the magnetic products could be used as raw materials for BF burdens, and tin was enriched in the non-magnetic materials.

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