Removing Tin from Tin-bearing Iron Concentrates with Sulfidation Roasting Using High Sulfur Coal

Yong YU, Lei LI* and Xiu-li SANG

State Key Laboratory of Complex Non-ferrous Metal Resources Clean Utilization, Engineering Research Center of Metallurgical Energy Conservation and Emission Reduction of Ministry of Education, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, 650093 China.

(Received on July 26, 2015; accepted on September 24, 2015; J-STAGE Advance published date: October 22, 2015)

With the sulfidation roasting process using high sulfur coal, the tin could be removed efficiently from tin-bearing iron concentrates, and the iron phase was reduced to metal iron. The research showed that the tin removal rate increased with roasting temperature and residence time. Different with the phenomena using pyrite as curing agent, deep reduction of tin-bearing concentrates did not cause tin removal rate decrease. The reason may be that curing rate of tin phases by the SO2 generated from high sulfur coal pyrolysis was higher, and the formation amounts of iron-tin alloy were decreased. The iron phase was mainly reduced into Fe from Fe2O3 and Fe3O4 in the roasting process. Tin content of the concentrates was decreased to 0.056% under the conditions of N2 flow rate of 60 ml/min, roasting temperature of 1 473 K, residence time of 60 min, high sulfur coal addition amounts of 70% and particle size of 200 meshes. The roasting product can meet the standard of BF ironmaking, which requires tin content in iron ores less than 0.08%. The work supplies a new approach for the clean use of high sulfur coal.

KEY WORDS: high sulfur coal; tin-bearing iron concentrates; sulfidation roasting; tin removal; comprehensive utilization of resources.

1. Introduction

With the rapid development of the Chinese iron and steel industry, large quantities of iron ores have been consumed. Low-grade, polymetallic and complex iron ores have taken an overwhelmingly dominant position in China nowadays. Realizing the sustainable development of iron and steel industry, China must use domestic resources above mentioned to produce a steady source of high-quality iron concentrates.

There is a typical iron ore containing tin, which is found in China of Neimenggu, Guangxi, Hunan and Yunnan.1) The tin impurity, mainly existing in the form of SnO2, reduces the iron products quality if it is not removed. At present, three methods of chlorination, reduction and sulfidation2,3) are mainly used to separate tin from tin-bearing iron concentrates. The tin is removed by the form of SnO in the method of reduction roasting, and tin content of the concentrates can be decreased lower than 0.01%. The process is difficult to be extended in industry due to its uneasy controlment. In the method of chlorination, tin phases are transformed to chlorides and evaporated making tin removal rate up to 94%, but the shortcoming is the corrosion to the facilities, enhancing the production cost and polluting the environment. In the process of sulfidation roasting, tin phases are mainly translated to SnS, and Sn is removed by making using of volatility difference between it with other components. Sulfidation roasting possesses the merits of low cost and adaptable material.

The reserve of high sulfur coal makes up approximately 30% of total coal reserves in China, and its mining proportion is demonstrating an annual increase.4) Burning high sulfur coal can cause the environment pollution by the large amounts of SO2 and NOx emission.5–7) Therefore, physical, microbial, chemical and pyrolytic methods for deep desulfurization have been studied.8,9) Methods of physical and microbial are not effective for removing organic sulfur. The chemical and pyrolytic methods can remove most sulfur, but they require rigorous operating conditions. It is necessary to find a new way for high sulfur coal short process use. Based on high S content in high sulfur coal and process requirements of sulfidation roasting, this research was carried out with high sulfur coal acting as reducing and curing agent for treating tin-bearing iron concentrates.

2. Experimental

2.1. Materials

Chemical composition of tin-bearing iron concentrates used in this study is presented in Table 1. It shows that iron content is 64.85% and tin content is 0.56%, both being well worth to be reclaimed. “Others” in Table 1 is mainly composed of O (existing as Fe2O3 and Fe3O4 etc.). Figure 1

* Corresponding author: E-mail: tianxiametal1008@163.com
DOI: http://dx.doi.org/10.2355/isijinternational.ISIJINT-2015-428
shows that main iron phases of tin-bearing iron concentrates are Fe$_2$O$_3$ and Fe$_3$O$_4$. Some researchers have proposed that main tin phases are SnO$_2$, and they are embedded in the iron phase. The industrial analysis composition of high sulfur coal used in this study is shown in Table 2, the sulfur content of which is 3.47%. In addition, chemical composition of the high sulfur coal ash is shown as Table 3.

### 2.2. Experimental Equipment and Method

The main equipment used in this work was an electric furnace with temperature ranging from 273 to 1873 K, and the temperature control precision was ±1 K. Zhang et al. found that external diffusion was not the rate controlling step when gas flow rate was above 60 ml/min, in view of which the N$_2$ flow rate is fixed at 60 ml/min in all experiments. High sulfur coal was used as reducing and curing agents in this study, and its addition amount was represented as quality ratio of high sulfur coal to tin-bearing iron concentrates. Four factors of roasting temperature, residence time, high sulfur coal addition amounts and particles were chosen for studying the effects on the tin removal rate from tin-bearing iron concentrates. All experiments were carried out in the electric furnace. At the start of the treatment, tin-bearing iron concentrates were crushed to less than 200 meshes, blended with a certain high sulfur coal and filled into a reactor. Subsequently, the electric furnace within the reactor was heated to the envisaged temperature under N$_2$ atmosphere. After a proper time held, the reactor was pulled out for cooling down and analysis.

### 2.3. Characterization

Chemical composition of the original and treated tin-bearing iron concentrates was analyzed by chemical analysis. Rigaku D/max-3B X-ray diffraction (XRD) was applied to investigate phase composition of the original and treated tin-bearing iron concentrates. Spectra were registered between 10 and 100 with a step of 8° and per step of 1 minute.

### 2.4. Calculations

In this research, the measured tin content was used to calculate the tin removal rate, which is defined as:

$$ R = \left(1 - \frac{w_{\text{Sn}_{\text{t}}}}{w_{\text{Sn}_{\text{o}}}}\right) \times 100\% $$

where $R$ is the tin removal rate, $w_{\text{Sn}_{\text{t}}}$ is tin content of the treated concentrates, $w_{\text{Sn}_{\text{o}}}$ is tin content of the original samples.

### 3. Mechanism Analysis

During the roasting process, tin phases were transformed to SnS and removed, and iron phases were reduced to Fe through controlling high sulfur coal addition amounts and roasting temperature.

#### 3.1. Mechanism of Tin Phase’s Sulfidation

Sulfur components in high sulfur coal can be divided into organic sulfur, pyritic sulfur and sulfate sulfur. In general, the functional groups of organic sulfur are divided into five kinds: mercaptan, sulfide, disulfide, containing thiophene ring aromatic system, and $\beta$-glucosinolates pyrone.

In Fig. 2, the DSC plot indicates that the pyrolytic reaction initiates at around 751.6 K. The first exothermic peak is observed at 751.6–827.0 K, and the second peaks at 1260.1–1295.8 K. The first exothermic peak probably corresponds to the pyrolysis of pyrite and unstable organic sulfur, and the second peak probably corresponds to the phase transition. MS plot indicates that there is also a SO$_2$ release peak at 1373 K, and it corresponds to decomposition of the stable organic sulfur. The SO$_2$ was found to be the main sulfur gases in the infrared detection (see Fig. 2). Compared with Sn, SnO$_2$ and SnO, the saturated vapor pressure of SnS is larger (see Fig. 3). Thus, the transform of tin phases to SnS is favorable to remove Sn. To make the transformation easier, the sulfidation roasting should be going under reducing atmosphere. It is generally believed that SnO undergoes a disproportionation reaction and forms Sn and SnO$_2$ shown as Eq. (2) when temperature is in the range of 673–1 313 K.

$$ 2\text{SnO} + \text{Sn} \rightarrow \text{SnS} + \text{SnO}_2 $$

Thus, sulfidation process of tin phases is divided into two stages as bellow.

$$ 1/2\text{SnO}_2 + \text{CO(g)} \rightarrow 1/2\text{Sn}(1) + \text{CO}_2(g) $$

$$ \text{Sn}(1) + \text{SO}_2(g) + 2\text{CO(g)} \rightarrow \text{SnS} + 2\text{CO}_2(g) $$
\[
\text{Sn}(l) + \text{SO}_2(g) + 2\text{H}_2(g) = \text{SnS} + 2\text{H}_2\text{O}(g) ...... (5)
\]

\[\text{T} > 1313 \text{K}\]

\[
\text{SnO}_2 + \text{CO}(g) = \text{SnO} + \text{CO}_2(g) \quad \text{.......... (6)}
\]

\[
\text{SnO}(g) + \text{FeS} = \text{SnS}(l) + \text{FeO} \quad \text{.......... (7)}
\]

\[
1/3\text{SnO}(g) + 1/3\text{SO}_2(g) + \text{CO}(g) = 1/3\text{SnS}(l) + \text{CO}_2(g) \quad \text{.......... (8)}
\]

\[
1/3\text{SnO}(g) + 1/3\text{SO}_2(g) + \text{H}_2(g) = 1/3\text{SnS}(l) + \text{H}_2\text{O}(g) \quad \text{.......... (9)}
\]

The standard Gibbs free energy changes as a function of temperature for these seven reactions are shown in Fig. 4. It can be seen that all reactions have minus values, and they are thermodynamically feasible. The tin removal is realized mainly through the interaction of CO and SO\(_2\) using high sulfur coal as curing and reducing agent.

### 3.2. Mechanism of Iron Phases Reduction

During the roasting process, the CO plays a major role for the iron phase’s reduction, and the related reactions are presented as follows:  \(^{15,16}\)

\[
3\text{Fe}_2\text{O}_3 + \text{CO}(g) = 2\text{Fe}_3\text{O}_4 + \text{CO}_2(g) \quad \text{.......... (10)}
\]

\[
1/4\text{Fe}_3\text{O}_4 + \text{CO}(g) = 3/4\text{Fe} + \text{CO}_2(g) \quad \text{.......... (11)}
\]

\[
\text{Fe}_3\text{O}_4 + \text{CO}(g) = 3\text{FeO} + \text{CO}_2(g) \quad \text{.......... (12)}
\]

\[
\text{FeO} + \text{CO}(g) = \text{Fe} + \text{CO}_2(g) \quad \text{.......... (13)}
\]

\[
\text{C} + \text{CO}_2(g) = 2\text{CO}(g) \quad \text{.......... (14)}
\]

Reactions (10)–(14) show that hematite is first reduced to magnetite, then to wustite, and finally to metallic iron in the roasting process. When reaction (14) reaches balance state, the final reduced product type mainly depends on roasting temperature. When roasting temperature is lower than 920 K, the system stability region is \(\text{Fe}_3\text{O}_4\) (see Fig. 5). With roasting temperature being in 920–958 K, the system stability region is \(\text{FeO}\). With roasting temperature being higher than 958 K, the system stability region is Fe. To make iron phases transfer to metallic iron at last, roasting temperature should be fixed at higher than 958 K, and the \(\text{P}_{\text{CO}}/(\text{P}_{\text{CO}} + \text{P}_{\text{CO}_2})\) higher than 58.15% (see the shaded part in Fig. 5). In our work, the \(\text{P}_{\text{CO}}/(\text{P}_{\text{CO}} + \text{P}_{\text{CO}_2})\) reached higher than 99% with Eq. (14) reaching equilibrium at 1473 K (see Fig. 5), and Sn phase’s reduction and \(\text{Fe}_2\text{O}_3\) reduction to Fe can be occurred simultaneously.  \(^{17}\)

![Fig. 2. Thermogram of high sulfur coal.](image)

![Fig. 3. Effects of temperature on vapor pressure of Sn, SnO, SnO\(_2\) and SnS.](image)

![Fig. 4. The standard free energy changes as a function of temperature for reactions (2)–(8).](image)

![Fig. 5. Predominance area phase diagram of Fe–C–O system.](image)
4. Results and Discussion

4.1. Effects of Roasting Temperature

Under N₂ flow rate of 60 mL/min, residence time of 60 min, high sulfur coal addition amounts of 70% and particle size of 200 meshes, seven roasting temperatures of 1 173, 1 273, 1 323, 1 373, 1 423, 1 473 and 1 573 K were chosen for studying the effects on the tin removal rate from tin-bearing iron concentrates.

Figure 6 shows that $R$ increases significantly from 39.28% to 90.00% with roasting temperature rising from 1 173 to 1 473 K. Temperature increase causes the boudol reaction (reaction(14)) to happen more violently, CO concentration to increase, SnO₂ reduction activation energy to reduce, and the overall reaction rate constant to increase. As a result, rates of tin phases sulfidation and removal both increase. In addition, the SnO can be generated through the SnO₂ reduction (see Eq. (6)) and it can exist stably with temperature being higher than 1 313 K. Its sulfidation extent is higher than SnO₂ and Sn, also being in favor of $R$ increase. The material is soft melting roasted at 1 573 K (see Fig. 7), causing escape of SnS being hindered, and the tin removal rate is decreased to 85%. In order to remove tin as much as possible, roasting temperature is fixed at 1 473 K.

4.2. Effects of Residence Time

Ten levels of residence time of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 min were respectively carried out to investigate the effects on the tin removal rate from tin-bearing iron concentrates.

Figure 8 shows that $R$ increases from 26.79% to 90.00% with residence time prolonging from 10 to 60 min, and increases little with residence time prolonging further. As previously mentioned, the SO₂ was found to be the main sulfur gas in the high sulfur coal pyrolysis process, and the tin removal reaction can be established as Eq. (15).

$$\text{SnO}_2 + 4\text{CO(g)} + \text{SO}_2(g) = \text{SnS} + 4\text{CO}_2(g) \quad \text{(15)}$$

Unreacted core shrinking model was chosen to describe the kinetics of Eq. (15), and the process can be divided into the following steps.19,20)

(I) CO and SO₂ diffuse through the gas boundary layer, and transfer to the surface of the tin-bearing iron concentrate;

(II) CO and SO₂ diffuse through the product layer to the reaction interface;

(III) Physisorption and chemisorption of CO and SO₂;

(IV) Chemical reaction at the product/reactant interface;

(V) Physidesorption and chemidesorption of SnS and CO₂;

(VI) SnS and CO₂ diffuse through the product layer to the surface of the gas boundary layer;

(VII) SnS and CO₂ diffuse through the gas boundary layer to the gas phase.

The reaction kinetic equations for different controlling steps are given in Table 4.21) In Table 4, $\alpha = \rho r_0^3 / KC_{n0}$, $b = r_0^2 \rho / 2D_{i0} C_{n0}$, $X = 1 - W/W_0$, $\rho$ is density of the solid reactant; $r_0$ is radius of the nuclear; $K$ is the reaction rate constant; $D_i$ is the diffusion rate constant; $\alpha_i$ is proportion rate of the interfacial chemical reaction; $b_i$ is proportion rate of the internal diffusion; $W_0$ is initial quality of the solid reactant; $W$ is quality of the solid reactant after t min; and t is the reaction time.
When using \(1 - (1 - X)^{1/3}\) as \(Y\)-axis and \(t\) as \(X\)-axis, the reaction is controlled by interfacial chemical reaction if there is a linear relationship between \(X\) and \(Y\). The results in Fig. 9 show excellent linear dependence between \(1 - (1 - X)^{1/3}\) and \(t\) in less than 50 min, indicating that the rate is controlled by the interfacial chemical reaction. Reactant concentrations decrease with residence time beyond 50 min, and the process is likely controlled by the combination of interfacial chemical reaction and gas internal diffusion.

If divided by \(1 - (1 - X)^{1/3}\), the kinetic equation of (18) can be simplified as

\[
t \frac{X^{1/3}}{1 - (1 - X)^{1/3}} = a_1 + b_1 \left[1 + (1 - X)^{1/3} - 2(1 - X)^{2/3}\right]
\]

When using \(1 + (1 - X)^{1/3} - 2(1 - X)^{2/3}\) as \(Y\)-axis and \(t\) as \(X\)-axis, the reaction rate is controlled by the combination of interfacial chemical reaction and gas internal diffusion if there is a linear relationship between \(X\) and \(Y\). The results in Fig. 10 show excellent linear dependence between \([1 + (1 - X)^{1/3} - 2(1 - X)^{2/3}]\) and \(t/\left[1 - (1 - X)^{1/3}\right]\), indicating that the rate is controlled by the combination of interfacial chemical reaction and gas internal diffusion. It causes that \(R\) increases little with residence time prolonging from 60 to 100 min. To decrease the process energy consumption and improve tin removal rate, residence time is fixed at 60 min.

### 4.3. Effects of High Sulfur Coal Addition Amounts

Five high sulfur coal addition amounts of 0%, 20%, 30%, 50% and 70% were chosen for studying the effects on the tin removal rate from tin-bearing iron concentrates. High sulfur coal addition amounts of 0% meant no high sulfur coal added but with coke replaced, and its carbon amount was equal to that 20% high sulfur coal addition.

**Figure 11** shows that \(R\) still reaches 14.28% with 0% high sulfur coal addition. The reason is that tin phases are reduced to SnO in the roasting process, and Sn can be removed in the form of SnO. With the increase of high sulfur coal addition from 0% to 20% (the same carbon amounts), \(R\) increases significantly from 14.28% to 70.00%. It indicates that the SO2 released from high sulfur coal pyrolysis has great promoting effect for the tin phases sulfide removal. When high sulfur coal addition amounts increase further from 20% to 70%, the CO pressure and sulfur potential of the reaction system increase, causing the sulfurization rate speeds up and \(R\) increases from 70.00% to 90.00%. In Fig. 11, \(R\) increases with high sulfur coal addition amounts all the time. Different with it, Li et al. found that tin removal rate decreased with anthracite addition amounts being over 10% using pyrite as curing agent, and the production of hardhead (Sn–Fe alloy) by deep reduction of tin-bearing iron concentrates was found to be the main reason. Compared with the pyrite, the SO2 has a greater sulfide activity and most tin phases can be sulphurized and removed before the formation of hardhead.

**Figure 12** shows that iron phases are mainly transferred to Fe, and no Sn–Fe alloy phase is detected. Over-reduction of tin-bearing iron concentrates using high sulfur coal doesn’t cause the tin removal rate decrease. To improve the tin removal rate, the
high sulfur coal addition amounts are fixed at 70%.

4.4. Effects of High Sulfur Coal Particle Size

Four high sulfur coal particle sizes of 40, 80, 100 and 200 meshes were chosen for studying the effects on the tin removal rate from tin-bearing iron concentrates. Figure 13 shows that R increases from 71.43% to 90% with high sulfur coal particle size decreasing from 40 to 200 meshes. Surface area of reaction particles increases as the particle size decreases, and it is beneficial to increasing the tin sulfidation and volatilization rates. To get rid of Sn as much as possible, the particle size is fixed at 200 meshes. Under this condition, Sn content of the tin-bearing iron concentrates decreases to 0.056%. It can meet the standard of BF ironmaking, which requires tin content in the iron ores less than 0.08%.

Acknowledgments

The authors wish to express thanks to National Science Fund for Distinguished Young Scholars (51304092) for financial support of this research.

REFERENCES