REVIEW ON KEY PARAMETERS DURING CARBOTHERMIC REDUCTION OF TIN FROM CASSITERITE

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Abstract

Due to the sudden sharp increase in tin demand, the production of tin through carbothermic reduction process requires refreshment by assembling important required data and disseminate to the potential producers. The current paper presents a review on different parameters that have been tested on different tin ores. Basicity, although simply defined as ratio between the basic oxides and acidic oxides, more information unfolds depending on whether the basic oxides or acidic oxides can be interchanged or replaced by another. The effects of interchanging a basic oxide by another on the kinetics and the slag composition and behaviors are discussed in the current paper. Since different ores have different compositions the adjustment of basicity may require different basic or acidic oxides. Different effects of such parameters on the carbothermic reduction of tin are here gathered and discussed.

Keywords: Metallurgy, carbothermic reduction, tin

1.   INTRODUCTION

The current high demand of tin and its accompanying metals Nb and Ta due to HighTech has revived the metallurgy of tin. The smelting of tin is essentially based on the carbothermic reduction. However, cassiterite being the main mineral carrying tin under oxide form has different composition depending on where it is mined. The most economic mineral in Sn-bearing ore is cassiterite (SnO_2). Sn production has increased for the past 30 years and 300000 tons per annum are produced in last years [1,2]. Prediction studies dictate that in the forthcoming years, the demand will be increased at a rate of 2% per annum for the next 5-10 years [1,3]. Sn is primarily produced from cassiterite ores and secondary sources (reprocessed materials) through the conventional mining, mineral processing and smelting processes. Conventional Sn smelting processes include use of air draught, reverberatory and electric arc furnaces which have the disadvantages of high smelting temperatures, long smelting time and high tin loss ratio (>10 wt%) [2]. Currently, Sn is efficiently recovered from its minerals by a carbothermic reduction process [1]. Several researchers have investigated on the reduction of cassiterite using a diverse of fluxing agents such as Silica and Lime [2]. The reduction of cassiterite may take place in the presence of gases such as CO and H_2 adjusted in a given ratio to promote the Boudouard reaction ($C + CO_2 \rightarrow 2CO$) and favour the reduction of SnO_2 to a Sn metal. For better overall recovery of tin, comminution followed by concentration is required to upgrade the run of mine. Some ores do contain valuable by-products, therefore a pre-concentration would be required.

1.1.   Pre-concentration of cassiterite ore bearing Nb-Ta minerals

Several equipments were used to concentrate Sn oxide. A shaking, sometimes associated with the spiral as a complementary equipment used for secondary concentration [4].

For a better pre-concentration, the following parameters must be optimized: inclination of the table, Stroke length, feed rate and water flow. The effect of shaking table on the beneficiation of cassiterite ore bearing

magnetite located on the eastern part of Egypt revealed that best separation was achieved when inclination of the table (4.13 degree), Stroke length (2.5 cm), feed rate (307.6 gm/min), and water flow rate (24.22 l/min). A concentrate having a grade of 13.2 wt% SnO_2 at a recovery of 86.2% by weight was achieved [5].

The presence of some oxides impacts negatively the recovery of tin and its physical properties. It is imperatively advised to design a smelting process where Sn is free of iron. Therefore, the removal of iron is very necessary during the extraction process.

1.2. Main reactions during tin carbothermic reduction

The different successive reactions that occur during carbothermic reductions are described as follows:

$$3SnO_2 \text{ (s)} + 2C \text{ (s)} = Sn_3O_4 \text{ (s)} + 2CO \text{ (g)} \tag{1}$$

$$3SnO_2 \text{ (s)} + 2CO \text{ (g)} = Sn_3O_4 \text{ (s)} + 2CO_2 \text{ (g)} \tag{2}$$

$$Sn_3O_4 \text{ (s)} + CO \text{ (g)} = 3SnO \text{ (s)} + CO_2 \text{ (g)} \tag{3}$$

The combination of reactions (2) and (3) leads to reaction (4a) or reaction (4b) below:

$$3SnO_2 \text{ (s)} + 3CO \text{ (g)} = 3SnO \text{ (s)} + 3CO_2 \text{ (g)} \tag{4a}$$

$$SnO_2 \text{ (s)} + CO \text{ (g)} = SnO \text{ (s)} + CO_2 \text{ (g)} \tag{4b}$$

$$SnO \text{ (s)} + CO \text{ (g)} = Sn \text{ (l)} + CO_2 \text{ (g)} \tag{5}$$

$$C \text{ (s)} + CO_2 \text{ (g)} = 2CO \text{ (g)} \tag{6}$$

With reaction (6) being the Boudouard reaction. It is known that the exothermicity of reduction reactions decrease with the valance of the metal. It is therefore, important to mention that from reaction (1) down to reaction (5) the heat released decreased.

2. EFFECTS OF DIFFERENT PARAMETERS

2.1. Effect of FeO/SnO ratio

Tin smelting occurs in two cycles namely primary and secondary cycle. In the primary cycle, cassiterite concentrates are smelted through carbothermic reduction. A crude tin and a slag are produced. The activity of FeO in the slag produced is lower than that of SnO. However, under strong reducing conditions FeO/SnO ratio can be increased leading to an increased Fe content in the metal. Recommendations are that the cooling rate be controlled to allow the hard tin to be concentrated at a specific point based on difference in temperatures as a driving force of purification [6]. The correlation between FeO and SnO in the slag is illustrated in **Figure 1** below. It transpires that SnO in the primary slag is inverse proportional to FeO in the slag. The optimum composition is said to be in the range of 30 to 40% FeO [6]. FeO and SnO are playing the role of fluxes.

The secondary cycle makes use of the primary cycle slag in addition to a reducing agent and CaO as a flux. The amount of CaO is limited to reduce the volume of the final slag since the volume of the reactor is limited. During carbothermic reduction of the primary slag, SnO and FeO are reduced to lower amounts.

In the secondary slag, SnO and FeO directly proportional which is opposite to the primary slag. When FeO increases, SnO increases though the proportionality is not as close as in the primary slag. An increase of 10 wt% of FeO leads to an increase of close to 2 wt% of SnO. However, an increase of 10 wt% of FeO in the primary slag leads to a decrease of more than 15% of SnO.

Besides the fact that this Sn smelting process has found success in the smelting industries, it had limitations of long smelting time and high operating temperature which make the process costly and high losses of Sn in the slag fraction. Some innovative approaches have been tested.
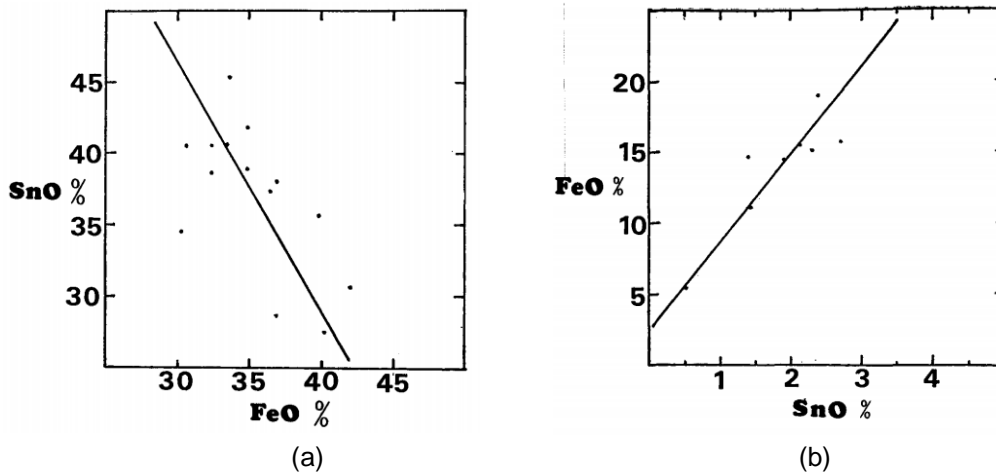
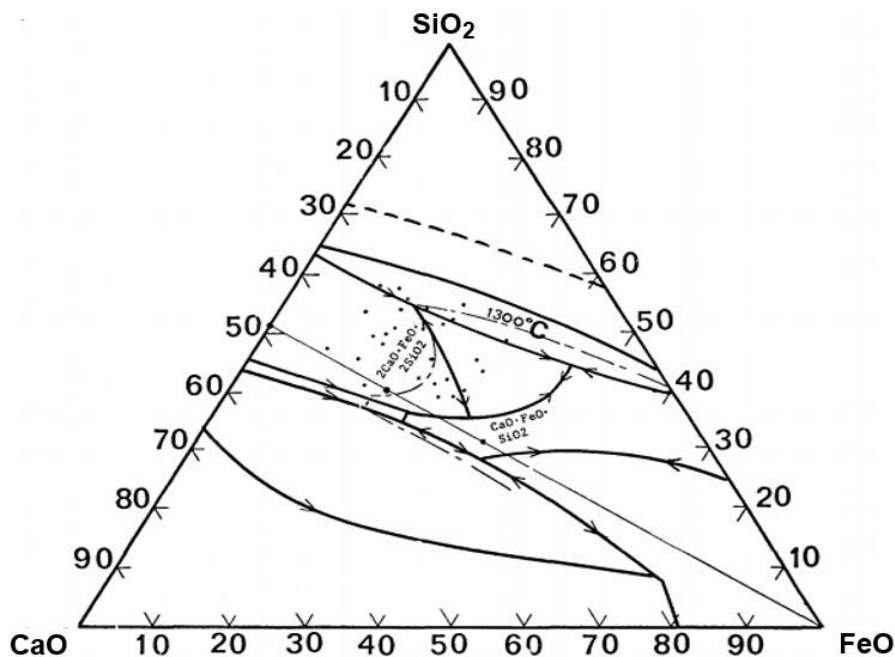**Figure 1** Relationship between SnO and FeO in the primary and secondary slags [6]

Figure 2 Ternary diagram CaO-SiO$_2$-FeO [6]

The ternary diagram in **Figure 2** provides enough information on the influence of CaO/SiO$_2$ ratio. It transpires that around 1300 °C, typical composition of the slag produced in the secondary is indicated around the liquidus line. It also shows the importance of CaO-SiO$_2$ ratio on the activities of FeO and SnO. This implies that for a low alumina and low MgO concentrate, the above ternary diagram can be of great contribution to predict and understand the quality of products during tin smelting.
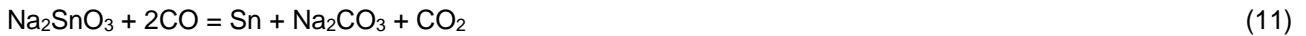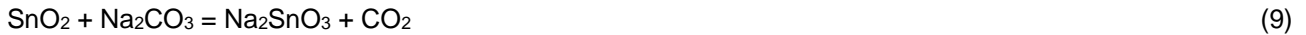
2.2. Effect of roasting on Sn recovery

An innovative approach to extract metallic Sn from cassiterite ore in presence of Na$_2$CO$_3$ was used in 2 steps [2]. The cassiterite ore was exposed to reduction roasting in the presence of Na$_2$CO$_3$ followed by water-leaching. During the reduction roasting, a huge amount of Sn metal was formed from SnO$_2$ while some of SnO$_2$ reacted with Na$_2$CO$_3$ to form a Na$_2$SnO$_3$ which is easily reduced to metallic Sn. Reactions involved during the whole process are summarized by the equation (7) to (13). About 98.1 wt% of the total Sn was recovered while

roasting at 950 °C with a carbon content of 80% of purity, for 120 minutes with a dosage of 30% of Na_2CO_3 according to the relationship ($Na_2CO_3/(SnO_2+SiO_2)$).

$$SnO + Sn = 2SnO \tag{7}$$

$$SnO + SiO_2 = SnO \cdot SiO_2 \tag{8}$$

Reduction in the presence of Na_2CO_3

$$SnO_2 + Na_2CO_3 = Na_2SnO_3 + CO_2 \tag{9}$$

$$SnO + Na_2CO_3 = Na_2SnO_3 + CO \tag{10}$$

$$Na_2SnO_3 + 2CO = Sn + Na_2CO_3 + CO_2 \tag{11}$$

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2 \tag{12}$$

$$2Na_2CO_3 + SnO.SiO_2 = Na_2SiO_3 + Na_2SnO_3 + CO \tag{13}$$

2.3.   Effect of Fe_3O_4 on reduction smelting of cassiterite

In case the cassiterite ore contains Fe_3O_4, the impact on Sn recovery in addition to the smelting temperature, time and the reducing agent, is the possible formation of Fe-Sn spinel during roasting [7]. However, this spinel can be reduced to Sn metal by smelting with strong reducing conditions. In case of weak reducing conditions, without changing the smelting time, the Sn metal may be formed whilst the increase in temperature plays a significant role for the formation rate Fe-Sn spinel. The amount of magnetite presented in a sample has a remarkable effect on the formation of new phases bearing SnO_2. The Sn/Fe ratio in the spinel is directly proportional to the cassiterite/magnetite mass ratio [7].

2.4.   Effect of basicity during reduction smelting of cassiterite

The basicity is always a useful parameter that govern the behavior of the slag. A basicity increases through addition of CaO and MgO while keeping MgO or keeping CaO constant plays an important role. The phases that form in the slag to preferentially collected Nb an Ta are similar when CaO and MgO are kept constant. However, the basicity increase leads to an increase in Sn recovery [8,9]. The change of basicity through the addition of Quartz has a significant effect during the reduction of cassiterite. The decrease of basicity on the Sn recovery has a negative impact. The addition of SiO_2 leads to the formation of orthosilicate phases such as $SnSiO_3$ [10]. This may constitute barriers around SnO particles, that decreases its activity disturbing the reduction mechanism of SnO to Sn [2]. **Figure 3** below summarizes the mechanism of reduction.
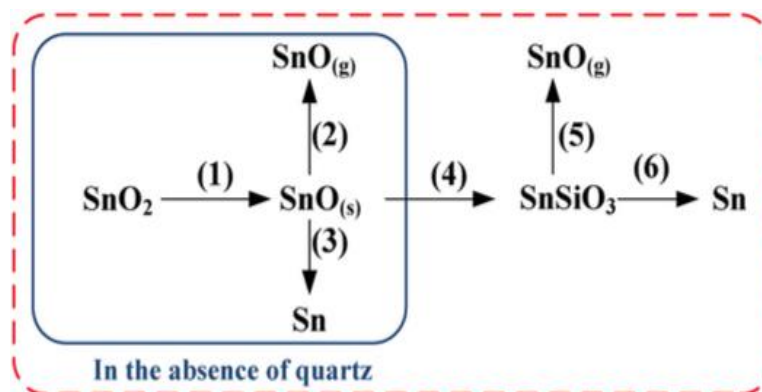

Figure 3 Influence of SiO_2 on tin production [2]

2.5.   Effect of carbon content during reduction smelting of cassiterite

The carbothermic reduction is the most known and popular method used in the smelting of Sn from cassiterite concentrates. This technique is applied on the Sn concentrate at temperature range 1200−1300 °C while

adding fluxes ($CaCO_3$, SiO_2) with the objective of producing an alloy containing 50–91% Sn. The smelting process takes place according to reaction 14.

$$2SnO_2 + 3C = 2Sn + 2CO + CO_2. \quad (\Delta G = 210 \text{ kJ/mol}) \tag{14}$$
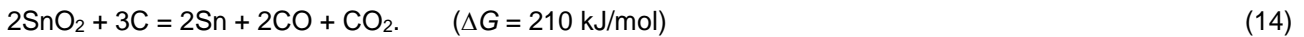
A series of previous studies have investigated on the use of carbon or carbon compounds such as $CaCO_3$, Na_2CO_3, K_2CO_3 during smelting process of cassiterite and columbotantalite mining tailings fluxed with borax while using graphite. A Sn metal of 96% purity was obtained using $CaCO_3$ as flux. It had about 25% of mass recovery compared to the feed concentrate while containing 45% of the overall Nb_2O_5/Ta_2O_5 [1].

Furthermore, the effect of carbon was also investigated on the reduction of SnO_2 from the anodic slime to produce a molten Sn. Han, et al., 2015 used a carbon source of 85 wt% fixed carbon and 15 % ash for the reduction process and found out that only 9 wt. % coke was needed to reduce SnO_2 slime to a high pure Sn metal at 1273 K. The quality of carbon has a positive effect on both the temperature as well as the metal quality.

The use of a combination of charcoal with Na_2CO_3-$NaNO_3$ on the reduction process of Egyptian cassiterite concentrate at temperature ranging 850-1000 °C was investigated. It was found that for 60 minutes of smelting, a Sn metal of 95% purity was obtained at 1000 °C further purification of Sn metal led to 99.6% [10].

The kinetics of the reduction reactions during the smelting of Sn oxide can be evaluated from the ratio of oxygen mass which is removed from the original sample over the total oxygen mass before any reduction process [3].

The effect of carbon from a gaseous source (CO) on the pretreated Sn compound at lower temperature was also investigated. The SnO_2 mineral was mixed with a salt of Na_2CO_3-$NaNO_3$ in the ratio of 1:0.3 to form an intermediate compound of Na_2SnO_3. After smelting for 1.5 hrs in the temperature range 600-950 °C while blowing CO gas, a Sn metal with 97% purity was obtained from the cassiterite concentrate [11].

In order to control the reduction rate, MgO content needs monitoring [3]. Due to the presence of K_2CO_3, SiO_2, Al_2O_3 and CaO the activation energy is reduced. The addition of MgO content during the reduction process has has a catalytic effect on the Boudouard reaction.

The conversion of SnO_2 into metal was found to be function of particle size, the type of reductant used, temperature and reaction time. It was noticed that effectiveness of collie coal was due to its high reactivity and its low ash content when compared to metallurgical coke [12].

During smelting it is important to well manage the slag. The saying:" look at the slag and the metal will look at it itself" is paramount. The viscosity of the slag and melting temperature of the slag are key for better slag/metal separation. The better the immiscibility of the two phases, the less metal carried or entrapped in the slag phase [13,14].

2.6.   Effect of time on phase formation in the slag during tin production

The reduction time plays an important role on the formation of phases dissolving some metals. In case the tin ore contains Nb and Ta oxides, at constant basicity, while varying reduction time at same working temperature, Nb and Ta are dissolved in monticellite, ferrocolumbite and fayalite. Tantalum oxide and Niobium oxide may reach 5% in the slag while the purity of metal reached a maximum of 99% of Sn and 1% Fe. This makes the slag of considerable value [9].

3.   CONCLUSION

Due to increasing demand of tin and its by-products, several parameters have to be considered based on the mineralogical composition of the ore. FeO/SnO ratio plays a critical role if a two-stage production flow sheet is adopted since the primary and secondary slag has an impact on tin recovery. Fe_3O_4 presence may reduce Sn

recover because of the formation of a spinel phase. Fe_3O_4 removal prior to the smelting is recommended. The basicity change through the addition of quartz decreases Sn recovery due to the formation of orthosilicates phases that decrease the activity of tin oxide while CaO addition improves Sn recovery coupled with formation of phases that collect Nb and Ta oxides if present in the ore. Roasting is key to improve Sn recovery The use of Na_2CO_3 has an impact on the slag formation by displacing SiO_2 that react with sodium carbonate to free tin oxide that consequently is efficiently reduced. In addition, the particle size plays also a critical role in the recovery of tin.

ACKNOWLEDGEMENTS

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