Reduction Roasting of Tin-Bearing Iron Concentrates Using Pyrite

Ren-jie ZHANG, Lei LI* and Yong YU

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.

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A novel method of reduction roasting of tin-bearing iron concentrates using pyrite (FeS_2) is proposed, in which hematite in tin-bearing iron concentrates is reduced to magnetite (Fe_3O_4) and cassiterite (SnO_2) is transformed to volatile tin sulphide (SnS). In a certain range, tin removal and iron reduction rates both increase with roasting temperature, pyrite amounts and residence time. When pyrite amounts exceed 5.00 mass%, some of the produced magnetite will be sulfurated to FeS and the evaporation of SnS (g) will also be obstructed. Tin content of the concentrate is decreased to 0.07 mass% and hematite is reduced to magnetite completely under the conditions of N_2 flow rate of $5.00 \times 10^{-6} \text{ m}^3/\text{s}$, roasting temperature of 1473.0 K, residence time of 60 min, pyrite addition amounts of 5.00 mass% and concentrates particle size of 0.075 mm. The roasting products can meet the standard of BF ironmaking, which requires tin content in iron ores less than 0.08 mass%, and the tin removed can be recycled through smoke dust collection.

KEY WORDS: pyrite; tin-bearing iron concentrates; reduction roasting; tin removal; comprehensive utilization of resources.

1. Introduction

In recent years, the Chinese iron and steel industry develops rapidly, and the corresponding iron ores external dependence degree has kept high for a long time, going against the industry further development. Besides, complex iron ores containing tin, vanadium, titanium and other nonferrous metals have taken an overwhelmingly dominant position in China nowadays.^{1–4)} Realizing sustainable development of the iron and steel industry, China must use domestic resources to produce a steady source of high-quality iron concentrates.

There is a tin-bearing iron ore which is mainly found in the north region of China.^{5,6)} Tin impurity reduces quality of the corresponding iron concentrates, and these concentrates cannot be used directly as blast furnace iron-making materials. Many approaches were reported to utilize these iron ores and the following findings were obtained. The process of iron ores treated by a joint physical separation process of grinding, reselection, magnetic separation and flotation could not obtain qualified iron concentrates, because tin phases (SnO_2) were embedded in iron phases and it was difficult for being separated through milling method.³⁾ In the methods of selective sulfurization or chlorination, tin could be effectively separated from iron ores, but the disadvantages which included equipment corrosion, environmental pollution, atmosphere and iron phases in the products hard to control were also apparent.^{4–12)} Using reduction method

to treat tin-bearing iron concentrates, tin contents of the products can be decreased lower than 0.01 mass%, but the process is difficult to be extended in industry due to its uneasy controlment.^{5–11)}

Pyrite (iron-pyrite, FeS_2) is the most widely used sulfidizer in the tin-containing materials treatment. The ferrous ion Fe^{2+} , element sulfur S, and the disulfide S_2^{2-} can be formed in the decomposition of pyrite,¹³⁾ and these products make pyrite possess reductive and sulfide property. Thinking of this, a novel method to reduce hematite in tin-bearing iron concentrates parallel to removing tin using pyrite has been proposed in this study. The tin removed can be recycled through smoke dust collection. Different with the earlier research, a special reductant, such as C, CO or H_2 ,^{5–11,14–17)} was not added to the reaction system. The treatment conditions, such as roasting temperature and time, pyrite addition amounts and particle size of the tin-bearing iron concentrates have been investigated.

2. Experimental

2.1. Sample Characterization

The tin-bearing iron concentrate used in this study was collected from a company in Yunnan province, China. Chemical composition (mass%) of it is depicted in **Table 1**. Table 1 shows that the major element present is iron (64.85 mass%) and tin content is of 0.27 mass%, both being well worth to be reclaimed. “Others” in Table 1 is mainly composed of “O” (existing as Fe_2O_3 and Fe_3O_4 etc.). Main mineral constituents of the samples, established by X-ray diffraction and EPMA, are reported in **Figs. 1** and **2**. Fig-

* Corresponding author: E-mail: tianxiametal1008@163.com
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ure 1 shows that main iron phases of the tin-bearing iron concentrates are Fe_2O_3 and Fe_3O_4 , and mass ratio of them is close to 1:1. Figure 2 also shows that the concentrates mainly contain hematite and magnetite, and minor amounts of cassiterite are embedded in iron phases at every size fraction. Pyrite was used as reducing agent and sulfidizer in the roasting process, the FeS_2 content of which is over 98.00 mass%.

2.2. Roasting Experiments

100 g of tin-bearing iron concentrates samples were used in every experiment, and addition amount of pyrite was calculated based on the quality ratio of it to tin-bearing iron concentrates, being range from 0.00 mass% to 100.00 mass%. After mixed carefully, the mixtures of tin-bearing iron concentrates and pyrite were roasted in a tube furnace in the range of 1 073.0–1 473.0 K under N_2 atmosphere. After a proper time held, the reactor was pulled out for cooling down and analysis.

2.3. Characterization

The thermo gravimetric analysis (TG) and differential

Fig. 1. XRD pattern of the tin-bearing iron concentrates.

scanning calorimetry (DSC) of the samples were performed on a thermal analyzer (NETZSCH, STA 449 F3). The typical measurements were performed at a heating rate of 0.17 K/s under Ar atmosphere. Chemical composition and mineralogy of the samples were characterized by chemical analysis, scanning electron microscope (SEM), point counting, energy dispersive spectrometer (EDS), and electron probe microanalysis (EPMA). All of the products phase compositions were detected by an X-ray diffraction (Rigaku D/max-3B) with a $\text{Cu-K}\alpha$ radiation. Spectra were registered between 10° and 90° with a step of 8° and per step of 1 minute. The thermodynamic data of species were given by FactSage thermochemical software. Mathematical expression of the tin removal rate was defined as:

$$R = \left(1 - \frac{M_T \times W_0}{M_C \times W_C} \right) \times 100\% \quad (1)$$

Where, M_C stands for the mass of tin-bearing iron concentrates used, W_C for the tin content in the origin tin-bearing iron concentrates, M_T for the total mass of the roasted residue, W_0 for the tin content in the roasted residue.

3. Thermo-chemical Behavior of the Mixture of Pyrite and Tin-bearing Iron Concentrates

It has been confirmed by many studies that the decomposition of pyrite proceeds through a multi-step process in the following sequence:^{18–20)}

The above results demonstrate that pyrite can be thermo-decomposed into pyrrhotite, troilite, and element sulfur during heat-treatment, all of which have the reduction ability to react with hematite.

Figure 3 shows TG-DSC curves of the mixture of tin-bearing iron concentrates and pyrite (addition amounts of 50.00 mass%) under Ar atmosphere. There are six endothermic peaks in the range of 323.3–1 558.3 K in addition to the dehydration stage approximately at 394.2 K. Each of these peaks corresponds to one weight-loss stage. At 703.8–864.0

Fig. 2. Mineral phase's distribution obtained by EPMA.

Table 1. Chemical composition of the tin-bearing iron concentrates (mass%).

Components	Fe	CaO	SiO ₂	Al ₂ O ₃	Sn	Sb	Pb	Zn	Cu	Others
Contents	64.85	1.55	0.91	0.87	0.27	0.34	0.06	0.04	0.01	30.07

Fig. 3. TG-DSC curves of the mixture of tin-bearing iron concentrates and pyrite (addition amounts of 50.00 mass%).

K, the pyrite breaks down to sulphur vapour and pyrrhotite,^{18–21)} corresponding to weight-loss of 5.72 mass%, and there is another weak endothermal peak as a shoulder appearing near 880.1 K, which is related to the reduction of hematite by the decomposed products of pyrite.¹⁹⁾ At 1 232.5–1 320.0 K, the weight-loss (–2.00 mass%) occurs and the corresponding endothermic peak is attributed to the further decomposition of the primary pyrrhotite before pyrite is completely decomposed.^{18–21)}

Reactions that may occur in temperature range of 950.0–1 558.3 K are listed as follows:^{19,22)}

Figure 4 shows standard Gibbs free energy changes of these reactions in temperature range of 323.3–1 558.3 K. It is known that the reduction of Fe_2O_3 by FeS_2 involves indirect (Eqs. (2) and (3)) and direct (Eq. (4)) ways.¹⁹⁾ It is seen from Fig. 4 that the Fe_2O_3 is reduced to Fe_3O_4 indirectly by FeS_2 above 703.4 K (Eq. (3)), and directly above 961.9 K. Besides, Fig. 4 shows that the initial temperature for sulfurization of SnO_2 to SnS (Eq. (5)) is about 956.8 K, and the reaction between FeS and SnO_2 (Eq. (6)) occurs hardly since FeS is stable below 1 558.3 K.

Enthalpy changes of the related reactions at temperatures of interest are plotted in Fig. 5, and some transitions during the reaction process (see Fig. 3) are found to be driven by enthalpy. The FeS undergoes a phase transformation from $\text{FeS}(\text{s})$ into $\text{FeS}(\text{l})$ theoretically starting at 1 463.0 K (see Fig. 5), as a result of which there is almost no change in weight but a strong exothermic peak at 1 423.2 K in Fig. 3. Based on the SnS theoretical phase transitions at 1 549.2 K in Fig. 5, $\text{SnS}(\text{l}) \rightarrow \text{SnS}(\text{g})$, the weight-loss of 3.17 mass% occurring in the range of 1 463.0–1 533.0 K shown in Fig. 3, may be attributed to the evaporation of $\text{SnS}(\text{g})$.

Fig. 4. The standard Gibbs free energy changes of reactions of (3)–(6) with temperature.

Fig. 5. Enthalpy changes of reaction of (3)–(6) with temperature.

4. Results and Discussion

In order to reduce hematite and achieve the purpose of removing tin, it is necessary to optimize the operating parameters of tin-bearing iron concentrates roasted with pyrite. For this purpose, the effects of roasting temperature, time, pyrite addition amounts and particle size of the tin-bearing iron concentrates were investigated.

4.1. Effects of Roasting Temperature and Time

Under N_2 flow rate of $5.00 \times 10^{-6} \text{ m}^3/\text{s}$, residence time of 60 min, pyrite addition amounts of 50.00 mass% and concentrates particle size of 0.075 mm, five roasting temperatures of 1 073.0, 1 123.0, 1 273.0, 1 373.0 and 1 473.0 K were chosen for studying the effects on the iron phases reduction and tin removal rate.

The pyrite decomposes into Fe_{1-x}S and S_x starting at 703.8 K (see Fig. 3), and the iron phase's reduction, shown as Eqs. (3) and (4), can be carried out at the roasting temperature (1 073.0–1 473.0 K) according to Fig. 4. XRD patterns of the roasted products at different temperatures are presented in Fig. 6 ('Unroasted' is tin-bearing iron concentrates without pyrite addition). It is obvious that temperature is an important factor for the reduction of hematite to

Fig. 6. XRD patterns of the roasted products at different temperatures.

Fig. 8. XRD patterns of the products roasted for different time.

Fig. 7. Effects of roasting temperature on the tin removal rate.

Fig. 9. Effect of residence time on the tin removal rate.

magnetite. Temperature increase improves the reaction rate between hematite and decomposed products of pyrite. The peak intensity of magnetite (reduction products) gradually increases and that of hematite decreases with temperature (see Fig. 6), and the transformation is basically completed when temperature reaches 1 473.0 K.

The pyrite cannot be further decomposed when temperature is relatively low,¹⁸⁾ and the formation of S is little, causing the tin removal reaction (Eq. (5)) also happens little at a low temperature. Figure 7 shows that tin removal rate increases slightly with temperature raised from 1 073.0 to 1 273.0 K, but it increases obviously to 64.29 mass% with temperature raised further to 1 473.0 K. At a higher temperature, the formation of tin sulphide (SnS) is promoted, and some SnS (l) can be transferred to SnS (g) which is easy to volatilize, both being favorable to increasing tin removal rate. In order to reduce hematite and remove tin as much as possible, roasting temperature is fixed at 1 473.0 K.

Figure 8 shows the hematite can partially be reduced into magnetite after being roasted for 40 min, and this transformation is completed with residence time prolonged further to 60 min. Figure 9 shows variations of tin removal rate as a function of roasting time. The tin removal rate increases gradually in the primary 60 min, from 1.79 mass% to 64.29

mass%, and then remains nearly constant. To decrease the process energy consumption and improve tin removal rate, residence time is fixed at 60 min.

4.2. Effects of Pyrite Amount

The FactSage 6.4 was used to calculate the equilibrium of roasted products in Gibbs free energy minimization under isothermal, isobaric and fixed mass conditions. Required data for computation were taken from FactPS database of the programme.

In Equilib program of FactSage, $\text{Fe}_2\text{O}_3(\text{s})$ (32.425 g), $\text{Fe}_3\text{O}_4(\text{s})$ (32.425 g), $\text{CaO}(\text{s})$ (1.55 g), $\text{SiO}_2(\text{s})$ (0.91 g), $\text{Al}_2\text{O}_3(\text{s})$ (0.87 g), $\text{SnO}_2(\text{s})$ (0.71 g), $\text{FeS}_2(\text{s})$ and $\text{N}_2(\text{g})$ were selected as reactant precursors, where $\text{N}_2(\text{g})$ was an inert gas to strict control the retained content of O_2 in the atmosphere. The calculations were performed in 100 g tin-bearing iron concentrates with variable pyrite amounts added under temperature of 1 473.0 K and atmosphere pressure of 1 atm. The phases of iron sulfide (FeS), magnetite (Fe_3O_4), hematite (Fe_2O_3), cassiterite (SnO_2), tin sulphide (SnS), sulfur dioxide (SO_2) and element sulfur (S_2) were assumed to be present in the roasted products and results of phase's equilibrium are present in Fig. 10. It shows that increase of pyrite amounts improves formation of Fe_3O_4 and SnS under

pyrite amounts less than 5.00 mass%. When pyrite amounts increase over 5.00 mass%, the Fe_3O_4 amounts decrease and FeS amounts increase obviously.

The mixtures of tin-bearing iron concentrates and pyrite at different quality ratios were roasted at 1473.0 K for 60 min. **Figure 11** shows that almost all diffraction peaks are assigned to magnetite when pyrite addition is 5.00 mass% and the FeS phase appears and increases with pyrite

Fig. 10. Equilibrium amounts of species in roasted products as a function of pyrite amounts.

Fig. 11. XRD patterns of the products with different pyrite addition amounts.

amounts from 5.00 mass% to 100.00 mass%. These results are in agreement with those obtained from Fig. 10. When pyrite amounts exceed 5.00 mass%, some of the produced magnetite will be sulfurated to FeS, as a result of which magnetite amounts decrease and FeS amounts increase.

Figure 12 shows that tin removal rate increases sharply with pyrite addition from 0.00 mass% to 5.00 mass% and remains nearly constant as pyrite addition increases further. $\text{SnO}_2(\text{s})$ can be transformed into $\text{SnS}(\text{g})$ completely based on the equilibrium-analysis (see Fig. 10), and there will be no tin residue observed in the roasted products if $\text{SnS}(\text{g})$ volatilizes completely. However, the max tin removal rate is only about 72.86 mass% in the roasting experiments (see Fig. 12).

With pyrite addition amounts of 50.00 mass%, the mixture was roasted at 1473.0 K for 60 min, and a scanning electron microscope provided with a detector of back scattered electrons (SEM-BSE) was used to characterize the products morphology. Some pictures were made (**Figs. 13(a)** and **13(b)**), and EDS analyses (**Fig. 14**) for the selected areas were performed. Some holes can be observed in the products morphology (see Fig. 13(a)), and the Fe–O, Fe–O–Sn–S, and Fe–S–O phases are found to be formed at the surface of these holes deduced from Figs. 13(b) and 14, appearing to be spherical particles. Taking into consideration of equilibrium-analysis and effects of pyrite amounts

Fig. 12. Effect of pyrite amounts on the tin removal rate.

Fig. 13. SEM photos of the roasted products with pyrite addition amounts of 50.00 mass%.

Fig. 14. EDS analyses of 1, 2 and 3 microareas of the SEM photos.

Fig. 15. XRD patterns of the roasted products at different particle sizes of tin-bearing iron concentrates.

Fig. 16. Effect of tin-bearing iron concentrates particle size on the tin removal rate.

on the tin removal rate, it could be stated that the formation of these holes is caused by the aggregation of gaseous SnS, SO₂ and S₂ within the mixture of iron sulfide (FeS) liquid and magnetite particles.^{23,24)}

In order to decrease the formation amounts of FeS which hinders the evaporation of SnS(g), pyrite addition amounts are fixed at 5.00%.

4.3. Effects of Particle Size

Surface area of reaction particles increases as the particle size decrease, and it is beneficial to increasing iron reduction and tin sulfidation rates. Figure 15 shows phase composition of the products with 5.00 mass% pyrite addition and roasted for 60 min at 1473.0 K, the results show that peak intensity of the magnetite increases obviously while tin-bearing iron concentrates average particle size decreases from 0.425 mm to 0.075 mm. Obviously, the effect of its particle size on the tin removal rate is very small (shown in

Fig. 16) due to its low content, although it has been changed during the reduction roasting process.

As discussed above, the optimum parameters are established as follows: roasting temperature, 1473.0 K; roasting time, 60 min; pyrite amounts, 5.00 mass%; particle size, 0.075 mm. After roasted, the hematite in tin-bearing iron concentrates can be reduced to magnetite completely, meanwhile, the tin content is decreased from 0.27 mass% to 0.07 mass% (tin removal rate of 72.86 mass%). The roasted concentrates can meet the standard of BF ironmaking, which requires Sn content in the iron ores less than 0.08 mass%.⁶⁾ Besides, the tin removed can be recycled through smoke dust collection. It indicates the decomposed products of the pyrite can pre-reduce hematite into magnetite and achieve the purpose of Sn effective removal from tin-bearing iron concentrates.

5. Conclusions

The reduction of hematite to magnetite and effective removal of Sn from the tin-bearing iron concentrates through co-roasting with pyrite are feasible. The factors including pyrite amounts, roasting temperature, residence time and particle size of tin-bearing iron concentrates have important influences. The hematite in tin-bearing iron concentrates can be reduced to magnetite directly by FeS_2 above 961.9 K and indirectly above 703.4 K. The initial temperature for sulfurization of SnO_2 to SnS is about 956.8 K using FeS_2 , and the reaction between FeS and SnO_2 occurs hardly since FeS is stable below 1 558.3 K.

In a certain range, the tin removal and iron phases reduction rates both increase with roasting temperature, residence time and pyrite amounts. When pyrite amounts exceed 5.00 mass%, some of the produced magnetite will be sulfurated to FeS and the evaporation of SnS (g) will be obstructed. As a result, magnetite formation and tin removal rate decrease. The optimum conditions are established as follows: roasting temperature, 1 473.0 K; roasting time, 60 min; pyrite amount, 5.00 mass%; particle size, 0.075 mm. After roasted under these conditions, the hematite in tin-bearing iron concentrates can be reduced into magnetite completely, meanwhile, the tin content is decreased from 0.27 mass% (unroasted sample) to 0.07 mass%. It can meet the standard of BF ironmaking, which requires Sn content in the iron ores less than 0.08 mass%, and the roasted concentrates can be used directly as blast furnace iron-making materials. In addition, the tin removed can be recycled through smoke dust collection.

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