Influence of Al₂O₃ on Equilibrium Sinter Phase in N₂ Atmosphere

Liaosha LI, Jibin LIU, Xingrong WU, Xue REN, Wenbin BING and Liushun WU

Anhui Provincial Key Laboratory of Metallurgical Engineering & Resources Recycling (Anhui University of Technology), Ma’anshan, Anhui, 243002, China. E-mail: liliaosha@sina.com

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1. Introduction

As the increasing utilization of Australia iron ore with high Al₂O₃ in BF in iron and steel factory, 1) the content of Al₂O₃ in sinter increased and brought up several negative influences on its metallurgical properties, 2–5) such as strength decreasing, RDI increasing, unsuitable changes of melting and drop points etc. N. V. Y. Scarlett et al. have studied the reaction sequences in the formation of silico-ferrites of calcium and aluminum (SFCA) in iron ore sinter. 6) X. R. Liu et al. have studied the mineralogical characteristics such as composition, microstructure and crystallographic characteristics of ferrite in low-temperature sinter. 7) Y. Wu has studied the effect of Al₂O₃ content of present sinter on its properties. 8) Other researchers also have made numerous valuable work on this, 9–11) but most of them focused on the process technology of sinter or iron making. Hitherto, most of essential mechanism is unclear. Especially, the distribution and behaviors of Al₂O₃ in sinter, with high level Al content, are unknown, which is the key to determine phase compositions and metallurgical properties of sinter. As the result, it leads to the difficulty to control its metallurgy process in BF.

Therefore, to make out the thermodynamic reasons of metallurgical property worsening of high Al-bearing sinter, it is necessary to investigate the distribution of Al and other elements in equilibrium phases of the sinter, which can provide the foundation to resolve the problems of Al-bearing iron ore sintering and metallurgy as well.

2. Experimental

2.1. Materials, Apparatuses and Equipments

Materials: The samples were synthesized based on the key component of sinter of Maanshan Iron and Steel Co., the content of Al₂O₃ changed from 1.5 mass% up to a top concentration of 4.0 mass% (Table 1).

All of the chemicals used in experiments such as Fe₂O₃, Fe₃O₄, SiO₂, MgO, Al₂O₃ were analytical reagent.

Apparatuses and Equipments: The main experimental equipment was a self-control style electronic high-temperature furnace with silicon molybdenum rods as heating element, an alumina crucible with experimental sample is closed in an corundum tube within the furnace, and an alumina supporter was used to keep the crucible in the isothermal zone.

The corundum tube was airproofed by a rubber plug with a porous alumina brick as an insulator. There was an inlet pipe and an exhaust pipe in rubber plug. The structural map of experimental equipment was shown in Fig. 1.

2.2. Experimental Procedure

According to Table 1, the raw materials were prepared and mixed for 40 min by a grinder and shaped in column samples with 12 mm diameter and 10 mm high in a press moulding machine. Each sample was put into an alumina crucible and heated to 1 610 K in self-control style electronic furnace for 10 h. Then, the samples were taken out when they were cooled down to 100°C at the furnace. The samples were under the nitrogen circumstances during experiments.

After above experiment, some samples were grinded down fine enough and characterized with X-ray diffraction (X’TRL made in Switzerland). The others were kept column shape, and polished sufficiently. After that, the samples were characterized with mineral phase-microscope (XTZ-1/1A) and SEM (PSVPS XL30 made in Dutch Philips) in order to obtain the microstructure, phase sizes and distributions of them. Mineral phase-microscope analysis data also provided the average statistical area of each mineral and the total observational scope area. According to the statistic results, the mineral volume ratio was calculated, which was supposed that area ratio of a mineral be equivalent with its volume ratio in point of statistic view. At last, the oxide compositions of minerals were characterized with EDS (EDAX XL30 made in America).

As expressed above, the samples with different contents of Al₂O₃ were characterized with XRD, microstructure analysis and mineral phase composition analysis.

Table 1. Chemical compositions of the samples (mass%).

| Sample No. | FeO | Fe₂O₃ | CaO | SiO₂ | MgO | Al₂O₃ |
|------------|-----|-------|-----|------|-----|-------|
| 1’         | 57.8| 8.5   | 9.8 | 4.7  | 2.4 | 1.5   |
| 2’         | 57.4| 8.5   | 9.8 | 4.7  | 2.4 | 2.0   |
| 3’         | 56.7| 8.5   | 9.8 | 4.7  | 2.4 | 3.0   |
| 4’         | 56.0| 8.5   | 9.8 | 4.7  | 2.4 | 4.0   |

Fig. 1. The structural map of experimental equipment. 1: exhaust pipe, 2: inlet pipe, 3: alumina crucible, 4: sample, 5: furnace mantle, 6: fundus, 7: rubber stop, 8: insulation brick, 9: corundum tube, 10: isothermal zone, 11: furnace box, 12: alumina brick, 13: temperature controlling system, 14: lead, 15: thermoscope for temperature controlling.
3. Results

3.1. XRD Analysis

The result of X-ray diffraction analysis of sample 1#, 1.5 mass% of Al₂O₃, was shown in Fig. 2(a). It can be seen that the main phases are magnetite and magnesio-ferrite solution, complex calcium ferrite solid solution with aluminum or SFCA, hematite and dicalcium silicate.

The XRD results of sample 3# were shown in Fig. 2(b) without distinct difference with the sample 1#. The main minerals were also magnetite and magnesio-ferrite solution, SFCA, hematite and dicalcium silicate.

3.2. SEM/EDS Analysis

Phase-microscope observation and SEM photo of the sample 1# and 3# were shown in Fig. 3 and Fig. 4, respectively. The both figures told that the sample consisted of four mineral phases mainly. Combined with EDS, “1” symbolized magnetite and magnesio-ferrite solution; “2” symbolized hematite; “3” was SFCA. “4” symbolized dicalcium silicate with a little iron. SFCA is the main mineral phase, which all Al₂O₃ was soluted in almost. Using EDS results in Table 2, the chemical formula calculated of SFCA within sample 1# was: 7.7CaO·13.6Fe₂O₃·Al₂O₃·3.4SiO₂. Besides, the chemical composition of SFCA within sample 3# could be determined as 4.8CaO·11.4Fe₂O₃·Al₂O₃·2SiO₂.

3.3. Mineral Compositions of Samples

Based on the phase-microscope analysis, the results of mineral compositions of samples were shown in Table 3. The relative ratio and element distributions for these minerals have changed.

As seen from Table 3, the compositions of main phase in equilibrium sinter with different Al₂O₃ level were magnetite and magnesio-ferrite solution, hematite, SFCA, and dicalcium silicate. Furthermore, the percentage of SFCA in-
increased as the rising of Al$_2$O$_3$ obviously in sinter, and made its composition change largely. In other side, as the rising of Al$_2$O$_3$ in sinter, the content of magnetite and magnesio-ferrite solution decreased greatly, but the ratio of hematite rarely changed, and dicalcium silicate ratio decreased slightly.

4. Discussions

4.1. Distribution and Behaviors of Al$_2$O$_3$ in Sinter

Based on the above and Table 3, all of Al$_2$O$_3$ concentrated in mineral of SFCA, no any Al$_2$O$_3$ appeared in other phases. Moreover, as the content of Al$_2$O$_3$ rising, the mineral of SFCA increased largely in sinter and the composition changed apparently with the formula changed from 7.7CaO·13.6Fe$_2$O$_3$·Al$_2$O$_3$·3.4SiO$_2$ to 4.8CaO·11.4Fe$_2$O$_3$·Al$_2$O$_3$·2SiO$_2$, when the percentage of Al$_2$O$_3$ was from 1.5 up to 3.0 in sinters. The relative ratio of Al$_2$O$_3$ and w$_{Al}$/w$_{Si}$ increased distinctly, while w$_{Ca}$/w$_{Si}$ decreased. It was suggested that the activity of Al$_2$O$_3$ increased with the content of Al$_2$O$_3$ rising for the system. In addition, because Al$_2$O$_3$ is similar to Fe$_2$O$_3$ greatly in property, the trend of Al$_2$O$_3$ combining with CaO was stronger than that of Fe$_2$O$_3$ in this system.

Therefore, driving due to chemical potential difference, Al$_2$O$_3$ migrated in simple calcium ferrite to form SFCA easily. For the same reason, SFCA was the main mineral of sinter with high level of Al$_2$O$_3$.

4.2. Effect of Al$_2$O$_3$ on Phase Compositions in Equilibrium Sintering

As mentioned above, the mineral of SFCA increased obviously as Al$_2$O$_3$ level rising in sinter, and the ratio of Al$_2$O$_3$ concentrated also increased distinctly. For the reasons of the sorts of main mineral unchanged, it was certain that the relative proportion was changed. That was why the metallurgy property of sinter was worsen.

4.2.1. Effect of Al$_2$O$_3$ Level Rising on the Magnetite in Sinter

Magnetite in equilibrium may be represented by (Fe$_3$O$_4$), the relative content of magnetite in equilibrium is decided by the activity of (Fe$_3$O$_4$) — a$_{Fe_3O_4}$. A thermodynamics equilibrium between (Fe$_3$O$_4$) and (Fe$_2$O$_3$) should be established in this system.

$$6(\text{Fe}_2\text{O}_3) = 4(\text{Fe}_3\text{O}_4) + \text{O}_2$$  \hspace{1cm} (1)

The equilibrium constant of this reaction is $K = (a_{Fe_3O_4})^{4}P_{O_2}/(P_{Fe_2O_3})^{6}$, which is a constant at a certain temperature, the $P_{O_2}$ is oxygen partial pressure and the $P^{p}$ is standard atmospheric pressure. When the oxygen potential is a constant, $a_{Fe_3O_4}$ and $a_{Fe_2O_3}$ have the same variation characteristics, such as nonanibiquity and homonymous, namely, $a_{Fe_3O_4}$ decreases with the decreasing of $a_{Fe_2O_3}$ and vice versa. As the content of Al$_2$O$_3$ in sinter rising, the ratio of mineral of SFCA increases distinctly. A great amount of Fe$_2$O$_3$ combines with it. The $a_{Fe_3O_4}$ in reaction (1) reduces, which directly causes the reduction of $a_{Fe_2O_3}$; therefore, magnetite in equilibrium mineral decreases distinctly. As can be deduced, when the oxygen potential is constant at high level Al$_2$O$_3$, the ferrous iron in sinter decreases obviously with the content of Al$_2$O$_3$ rising. If adequate ferrous iron is kept, a certain oxygen potential should be decreased, and coal should be added properly.

4.2.2. Effect of Al$_2$O$_3$ Content Rising on the Dicalcium Silicate in Sinter

Dicalcium silicate, soluted a little ferrous iron in equilibrium sintering, reduced slightly with Al$_2$O$_3$ rising of sinter. With the content of Al$_2$O$_3$ rising in sinter, SFCA increased because of Al$_2$O$_3$ added combined with CaO and SiO$_2$ in the raw materials. As a result, the binding phase in sinter decreased, which probably caused the strength of sinter turning lower.

5. Conclusions

The equilibrium phase structure of sinter in different contents of Al$_2$O$_3$ was studied under N$_2$ atmosphere. The results showed that the sorts of mineral phase were unchanged with Al$_2$O$_3$ rising in sinter, but the relative proportion and chemical composition of the minerals changed. The main results were as follows:

(1) In equilibrium phases of sinter, Al$_2$O$_3$ from origin material mostly existed in the phase of SFCA.

(2) In equilibrium phases of sinter, the content of Al$_2$O$_3$ in sinter rising caused the phase of SFCA increased. At the same time, the content of magnetite reduced distinctly.

(3) In equilibrium phases of sinter, as the content of Al$_2$O$_3$, in sinter rising, the chemical component of SFCA changed apparently. Its chemical formula changed from 7.7CaO·13.6Fe$_2$O$_3$·Al$_2$O$_3$·3.4SiO$_2$ to 4.8CaO·11.4Fe$_2$O$_3$·Al$_2$O$_3$·2SiO$_2$ when the percentage of Al$_2$O$_3$ was from 1.5 up to 3.0.

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