Reaction between CaO and Fe₃O₄ under CO–CO₂ Atmosphere at 800°C–1 100°C

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(Received on July 24, 2016; accepted on September 5, 2016)

A considerable amount of works were focused on the formation mechanism of calcium ferrite phases during the iron ore sintering process, especially under various O₂ content atmospheres at temperatures higher than 1 100°C. But little attention has been paid on reactions between CaO and iron oxides in CO–CO₂ atmospheres at lower temperatures. In this study, the solid state reaction mechanisms between CaO and Fe₃O₄ under CO–CO₂ atmospheres at 800°C–1 100°C were revealed by using XRD, VSM, *etc.* The results indicated that Ca₂Fe₂O₅ was easily formed under 5–50 vol% CO/(CO+CO₂) atmosphere above 850°C via the reaction of $6\text{CaO} + 2\text{Fe}_3\text{O}_4 + \text{CO}_2 = 3\text{Ca}_2\text{Fe}_2\text{O}_5 + \text{CO}$ and the reaction would be promoted with increasing the roasting temperature. In the CO–CO₂ atmosphere, Fe₃O₄ is easily oxidized to Fe₂O₃ in the presence of CaO because CO₂ components act as oxidative medium for the oxidation of Fe²⁺ to Fe³⁺.

KEY WORDS: calcium ferrite; phase transformation; solid state reaction; iron oxide; calcium oxide.

1. Introduction

It is well known that calcium ferrites (CaO·2Fe₂O₃, CaO·Fe₂O₃ and 2CaO·Fe₂O₃) formed during the iron ore sintering process can improve the mechanical strength and the reducibility of the sinters.^{1–3)} A considerable amount of works were focused on the structure characterization and formation mechanism of calcium ferrite phases during the sintering process under various O₂ content atmospheres at the temperatures higher than 1 100°C.^{4–10)} Generally, solid state reactions and phase constitutions during the sintering process can be thermodynamically predicted using the equilibrium phase diagram. However, the phase transformation process at lower temperatures will be different from the predicted phase. And little attention has been paid on the reaction between CaO and Fe₃O₄ under CO–CO₂ atmosphere at 800°C–1 100°C, and it is uncertain whether CaO·xFe₂O₃ is formed under these conditions.

High calcium type tin, iron-bearing tailing is recognized as one of typically complex iron ore resources in China. Our previous researches indicated that the iron mineral in the tailings was goethite, while calcite was the main gangue minerals.¹¹⁾ A process of magnetizing roasting followed by magnetic separation was efficient to recover iron values from the tailings, and the calcium and tin-bearing minerals were separated into non-magnetic materials. Nevertheless, the iron recovery decreased obviously as the roasting temperature was higher than 850°C, and the effect of CaO on the phase transformation of iron oxides was still unclear. Previous researches have studied more about the convert of iron oxides during the magnetizing roasting process,^{11–14)}

but few researchers have studied the effect of gangue compositions (such as CaO and SiO₂) on the phase transformation of iron oxides.

Thus, the major objectives of this study was: 1) to investigate the reaction behaviors between CaO and Fe₃O₄ under CO–CO₂ atmosphere at 800°C–1 100°C; 2) to determine the effect of CaO on the iron recovery during the magnetizing roasting process; 3) to reveal the effect of CO–CO₂ atmosphere on the redox reactions of iron oxide in the present of CaO by using X-ray diffraction (XRD), Vibrating Sample Magnetometer (VSM), FactSage phase diagram analysis, *etc.*

2. Materials and Method

2.1. Materials

The high calcium iron tailings used in this study were taken from Yunnan Province, China.¹¹⁾ The main chemical compositions given in **Table 1** were determined by XRD. The XRD pattern of the sample is presented in **Fig. 1**. It can be seen from Table 1 that the total iron grade (T.Fe) of the sample was 35.53 wt%. The main impurities compositions included 14.75 wt% CaO, 5.72 wt% MgO, 1.74 wt% SiO₂ and 1.24 wt% Al₂O₃. As shown in Fig. 1, the iron exists as the form of goethite, and main gangue minerals are calcite and dolomite.

Analytic reagents of CaO and Fe₃O₄ with the purity beyond 99.9 wt.% (supplied by Aladdin, Shanghai) were

Table 1. Chemical compositions of the tin-, iron-bearing tailings.

Components	TFe	SiO ₂	Al ₂ O ₃	CaO	MgO	Sn	P	S	LOI
Content (wt%)	35.53	1.74	1.23	14.75	5.72	0.56	0.03	0.55	14.67

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DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-455>

Fig. 1. XRD pattern of the high calcium iron tailings.

also used in this study. And the purity of gases (CO , CO_2 and N_2) used for the roasting tests was higher than 99.99 vol.%.

2.2. Methods

All the simulative magnetizing roasting tests were conducted in a horizontal resistance furnace. A schematic diagram of the experimental equipment has been reported previously.^{11,15)}

The high calcium iron tailings were firstly mixed with 0.5 wt.% bentonite, and balled into 8 mm diameter green pellets in a $\Phi 1000$ mm disc pelletizer. Then, the green balls were dried in an oven at 105°C for 4 h. After that, the dried pellets were weighed and put into a corundum crucible. The corundum crucible carrying with dried pellets was straightly placed in the high temperature zone of the horizontal furnace. The total flow rate of the inlet mixed $\text{CO}-\text{CO}_2$ gas was fixed at 4.0 L/min. Next, the pellets were subjected to magnetizing roasting at a given temperature for 60 min. After that, the pellets were rapidly taken out and quenched into liquid nitrogen in order to prevent the re-oxidation of the roasted products. The roasted products were subjected to wet-grinding in a ball mill (Conical ball mill of XMQ $\Phi 240 \times 90$ mm) for 10 min and the grinding concentration (the mass fraction of grinding material on the total mass of the slurry) was fixed at 50 wt%, the mass percentage of the ground samples with a granularity below 0.075 mm was found as more than 80 wt%. Then the samples were followed by magnetic separation in a magnetic separator (Davis magnetic tube of XCGS-73) with a magnetic field intensity of 0.10 T. At last, the magnetic and non-magnetic materials were dried, weighted precisely and finely ground to 100 wt% less than 0.074 mm for chemical analysis.^{16,17)}

3. Results and Discussion

The effect of roasting temperature and CO content on the iron recovery were first examined. The CO content refers to the CO volume concentration in the $\text{CO}-\text{CO}_2$ mixed gas (*i.e.*, $\text{CO}/(\text{CO}+\text{CO}_2)$). In the experiments, the roasting time was fixed at 60 min, the particle size of the ground sample with a granularity below 0.075 mm was found as more than 80 wt%, and the magnetic field intensity was 0.10 T. The results listed in Table 2 indicated that the roasting tem-

Table 2. Effect of roasting conditions on the iron recovery of the high calcium iron tailings.

Roasting conditions		Evaluation indices of magnetic concentrate	
Temp/ $^\circ\text{C}$	CO content/vol%	Iron grade/wt%	Recovery of iron/wt%
850	30	65.4	71.0
	20	65.7	90.9
	15	67.3	91.6
	10	67.2	92.5
	5	67.0	93.3
	2	66.5	88.7
	600	65.2	76.1
	700	65.8	82.5
	800	66.9	87.8
	850	67.0	93.3
900		66.8	83.5
1 000		65.2	70.2

perature and CO content have obvious effects on the iron recovery. Optimal roasting conditions should be fixed at CO content of 5–15 vol% and roasting temperature of 850°C , and a magnetic concentrate containing more than 67 wt% TFe with an iron recovery over 87 wt% was obtained. However, the iron recovery decreased sharply when the roasting temperature was higher than 850°C .

3.1. Phase Transformation of the High Calcium Iron Tailings during the Roasting Process

In this section, the phase transformation and magnetism changes of the roasted products were analyzed by XRD (D/max 2550PC, Japan Rigaku Co., Ltd, Japan) and VSM (Vibration sample magnetometer, BHV-50HTI, Riken Keiki, Japan).

3.1.1. XRD Analysis

The effect of CO content varying from 2 vol% to 40 vol% on the phase transformation of the tailings was investigated and the XRD patterns of the roasted products were presented in Fig. 2. As seen from Fig. 2, the predominant iron mineral in the products was magnetite (Fe_3O_4), which suggested that the vast majority of goethite were converted to magnetite under $\text{CO}-\text{CO}_2$ atmosphere at 850°C . Nevertheless, the newborn magnetite would be over-reduced to wustite (FeO) when the CO content reached 40 vol%. And the diffraction peaks of calcite (CaCO_3) were weakened and disappeared as the CO content increased from 2 vol% to 5 vol%.

Figure 3 demonstrates the XRD patterns of the roasted products under the temperatures varying from 800°C to $1\,000^\circ\text{C}$. It was shown in Fig. 3 that the major mineral constituents in the products were magnetite, dicalcium ferrite, periclase, calcite and lime. With the temperature increasing from 800°C to $1\,000^\circ\text{C}$, the diffraction peak intensity of calcite decreased, while that of the lime increased significantly, indicating that higher roasting temperature promoted the decomposition of CaCO_3 . Besides, Fig. 3 illustrated that the diffraction peaks of dicalcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) increased

Fig. 2. XRD patterns of products roasted at different CO contents (roasting temperature of 850°C, roasting time of 60 min).

Fig. 3. XRD patterns of products roasted at different roasting temperatures (CO content of 5 vol%, roasting time of 60 min).

sharply as the temperature increased higher than 850°C. The results mentioned above indicated that the $\text{Ca}_2\text{Fe}_2\text{O}_5$ was formed even in a CO-CO_2 atmosphere, and the increase of temperature promoted the reaction between the iron oxide and CaO . The formation mechanism of $\text{Ca}_2\text{Fe}_2\text{O}_5$ under CO-CO_2 atmosphere is unclear and will be discussed in detail in Section 3.2.

3.1.2. VSM Analysis

In order to further study the effect of roasting temperature and CO content on the phase transformation of iron oxides, the magnetic hysteresis loops of the products roasted under different conditions were analyzed by VSM and the results are shown in Figs. 4 and 5. The results indicated that the magnetic property of the roasted products changed obviously with the increase of CO content and roasting temperature.

As presented in Fig. 4, the saturation magnetization (M_s) of raw tailings was only 0.51 emu/g, so it was almost impossible to recover the iron oxides by magnetic separation process. The M_s value of the roasted products markedly

Fig. 4. The magnetic hysteresis loops of the products roasted under different CO contents (Roasting temperature of 850°C, roasting time of 60 min).

Fig. 5. The magnetic hysteresis loops of the products roasted at different roasting temperatures (CO content of 5 vol%, roasting time of 60 min).

increased to 53.07 emu/g when the CO content was 5 vol%, and then it decreased obviously with the further increase of CO content. Optimal CO content was recommended as 5 vol%, and the results proved that a higher CO content caused the over-reduction of magnetite, which led to the decrease of iron recovery as listed in Table 2.

It can be seen from Fig. 5 that roasting temperature also has pronounced influence on the saturation magnetization of the roasted products, and properly increasing the roasting temperature is beneficial to increase the M_s value and the iron recovery. But exorbitant temperature could result in the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ and the decrease of M_s value, which was unfavorable for the iron recovery. The changing rule of M_s is in accordance with the results given in Table 2.

3.2. Reactions between CaO and Fe_3O_4 under CO-CO_2 Atmosphere

Figure 3 indicated that the $\text{Ca}_2\text{Fe}_2\text{O}_5$ was easily formed under CO-CO_2 atmosphere above 850°C, which decreased the iron recovery. It was known that the rate of gas-solid reaction was much greater than that of the solid-solid reaction. Hence, it can be concluded that the reduction of Fe_2O_3

to Fe_3O_4 should be prior to the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$, and the reactions between CaO and Fe_3O_4 under CO-CO_2 atmosphere should be further investigated.

In order to exclude the negative influence of the gangue minerals in the tailings, analytic reagents of CaO and Fe_3O_4 were used to prepare the tested samples as mole ratio of 2:1 ($\text{CaO}:\text{Fe}_3\text{O}_4$). All of the reagents were pre-ground until the particle size passing through a 0.074 mm sieve, and the samples were mixed up gently with an agate mortar and pestle for 30 min. Then, the mixed samples were roasted at the given temperature under CO-CO_2 atmosphere for 60 min. At last, the roasted sample was analyzed by XRD and chemical analysis method.^{16,17)}

3.2.1. Thermodynamics Analysis

It was known that Fe_3O_4 could exist stably under 5 vol% CO content.¹¹⁾ The thermodynamic analysis of $\text{Fe}_3\text{O}_4\text{-CaO}$ system under 5 vol% $\text{CO}/(\text{CO}+\text{CO}_2)$ atmosphere was firstly performed using FactSage thermo-chemical software and the result is presented in Fig. 6.¹⁸⁾ Figure 6 demonstrated that $\text{Ca}_2\text{Fe}_2\text{O}_5$ existed in the $\text{Fe}_3\text{O}_4\text{-CaO-CO-CO}_2$ system when the temperature was higher than 760°C . The final phase constitutions of the products were determined by the mole ratio of $\text{Fe}_3\text{O}_4/(\text{CaO}+\text{Fe}_3\text{O}_4)$, Fe_3O_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$ were stable when the ratio was higher than 0.25 at $760\text{--}1130^\circ\text{C}$. Therefore, the reaction of $\text{CaCO}_3=\text{CaO}+\text{CO}_{2(g)}$ was suppressed by the partial pressure of CO_2 , and the decomposition temperature of CaCO_3 was about 890°C . And two regions of ($\text{CaO}+\text{Ca}_2\text{Fe}_2\text{O}_5$) and ($\text{CaCO}_3+\text{Ca}_2\text{Fe}_2\text{O}_5$) were found in Fig. 6 when $\text{Fe}_3\text{O}_4/(\text{CaO}+\text{Fe}_3\text{O}_4)$ mole ratio was lower than 0.25. The results in Fig. 6 indicates that $\text{Ca}_2\text{Fe}_2\text{O}_5$ can exist stably under 5 vol% $\text{CO}/(\text{CO}+\text{CO}_2)$ content. However, the chemical valence of iron in $\text{Ca}_2\text{Fe}_2\text{O}_5$ is 100% Fe^{3+} while that in Fe_3O_4 is 66.7% Fe^{3+} and 33.3% Fe^{2+} . And the oxidation reaction of Fe^{2+} to Fe^{3+} under CO-CO_2 atmosphere will be discussed in the next section.

3.2.2. The Reaction Mechanism between CaO and Fe_3O_4

It was found that the decrease of the iron recovery was attributed to the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$. Therefore heat treatment experiments with using pure CaO and Fe_3O_4

were performed at 1000°C . The effect of CO content on the reactions between CaO and Fe_3O_4 was first studied and the XRD patterns of the roasted samples are demonstrated in Fig. 7. It was shown in Fig. 7 that the major mineral constituents in the products were dicalcium ferrite, magnetite and wustite. With the increase of CO content from 5 vol% to 50 vol%, the diffraction peaks of $\text{Ca}_2\text{Fe}_2\text{O}_5$ were almost unchanged, which indicated that $\text{Ca}_2\text{Fe}_2\text{O}_5$ was stable under 5–50 vol% CO content. Only a small amount of Fe_3O_4 was reduced to FeO when CO content varied between 20 vol% and 50 vol%.

The effect of roasting temperature on the phase transformation of CaO and Fe_3O_4 mixtures is given in Fig. 8. As seen from Fig. 8, the diffraction peaks intensity of $\text{Ca}_2\text{Fe}_2\text{O}_5$ was almost indiscernible at 850°C , and CaO and Fe_3O_4 were found as the main phases in the products. As the roasting temperature increased to 900°C , the diffraction peaks of $\text{Ca}_2\text{Fe}_2\text{O}_5$ were enhanced remarkably. $\text{Ca}_2\text{Fe}_2\text{O}_5$ was the main phase when the roasting temperature further increased to $1000\text{--}1100^\circ\text{C}$, and the diffraction peaks of CaO and

Fig. 7. XRD patterns of the products roasted at different CO contents (roasting temperature of 1000°C , roasting time of 60 min).

Fig. 6. Phase diagram of the $\text{Fe}_3\text{O}_4\text{-CaO-CO-CO}_2$ system under 5 vol% $\text{CO}/(\text{CO}+\text{CO}_2)$ atmosphere.

Fig. 8. XRD patterns of the products roasted at different temperatures (CO content of 5 vol%, roasting time of 60 min).

Fe_3O_4 decreased obviously. The results indicated that higher temperature promoted the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$, and the optimal roasting temperature should be not higher than 850°C , which was in accordance with the previous results presented in Table 2.

Figure 9 presents the classical gas-phase equilibrium diagram of FeOx under $\text{CO}\text{--}\text{CO}_2$ atmosphere, the shadow region (steady existence of Fe_3O_4) shows the suitable theoretical conditions for realizing the magnetization of iron oxides. In order to further determine the iron chemical state of Fe^{2+} content and T.Fe (total iron content of Fe^{2+} and Fe^{3+}) in the roasted products, Sample 1# to Sample 7# (shown in Figs. 7 and 8) were analyzed by chemical analysis methods. $\text{Fe}^{2+}/\text{T.Fe}$ values and $\text{Fe}^{3+}/\text{T.Fe}$ values are calculated and display in **Table 3**. Furthermore, theoretical calculation iron valence states under the same condition marked in Fig. 9 (Point a–g) are also demonstrated in Table 3.

As shown in Fig. 9 and Table 3, Points a and b were in the stability zone of FeO , and the theoretical values of $\text{Fe}^{2+}/\text{T.Fe}$ and $\text{Fe}^{3+}/\text{T.Fe}$ were 100 wt% and 0 wt%, respectively. Points c to g were located in the stability zone of Fe_3O_4 , while the theoretical values of $\text{Fe}^{2+}/\text{T.Fe}$ and $\text{Fe}^{3+}/\text{T.Fe}$ were 66.7 wt% and 33.3 wt%, respectively.

However, the $\text{Fe}^{3+}/\text{T.Fe}$ values of Sample 1# to Sample 4# in the present of CaO were much higher than the theoret-

cal values, which indicated that Fe^{2+} in Fe_3O_4 was partially oxidized to Fe^{3+} to form $\text{Ca}_2\text{Fe}_2\text{O}_5$. It is worthy to note that $\text{Ca}_2\text{Fe}_2\text{O}_5$ could be formed even under 50 vol% CO content (Sample 1# in Fig. 7), and the $\text{Fe}^{3+}/\text{T.Fe}$ value was as high as 80.2 wt%. The results in Table 3 (Sample 4# to 7#) also indicated that, the $\text{Fe}^{3+}/\text{T.Fe}$ value increased as the increasing of roasting temperature under 5 vol% CO content.

The results suggested that CO_2 components in the 5–50 vol% $\text{CO}/(\text{CO}+\text{CO}_2)$ atmosphere act as oxidizing agent in the present of CaO , because $\text{Ca}_2\text{Fe}_2\text{O}_5$ was a very stable phase under this condition, and the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ promoted the oxidation reaction of Fe^{2+} to Fe^{3+} .

In order to investigate the reaction mechanism between CaO and Fe_3O_4 even further, mixture of CaO and Fe_3O_4 was roasted under high purity nitrogen atmosphere at $1\,000^\circ\text{C}$ for 60 min, and the XRD pattern of the roasted sample is shown in **Fig. 10**. It was found that the main phases in the samples were dicalcium ferrite, magnetite, lime and wustite.

On the basis of the results mentioned above, the reaction mechanism between CaO and Fe_3O_4 under $\text{CO}\text{--}\text{CO}_2$ atmosphere can be concluded as follows: first, CaO reacts with Fe_3O_4 as Eq. (1), because $\text{Ca}_2\text{Fe}_2\text{O}_5$ and FeO are found in the roasted samples as shown in Fig. 10. Then, FeO would be oxidized to Fe_3O_4 as Eq. (2), because FeO can't exist stably under the conditions of the shadow region as shown in Fig. 9.

Fig. 9. Gas-phase equilibrium diagram of FeOx under $\text{CO}\text{--}\text{CO}_2$ atmospheres.

Fig. 10. XRD patterns of CaO and Fe_3O_4 mixtures roasted under high purity nitrogen (99.999 vol%) (roasting temperature: $1\,000^\circ\text{C}$, roasting time: 60 min).

Table 3. Chemical valence state analyses of iron in the roasted samples.

Roasting conditions			In the present of CaO (Samples in Figs. 7 and 8)		Point.	In the absence of CaO (Theoretical calculation in Fig. 9)	
Temp/ $^\circ\text{C}$	CO content/vol%	Test NO.	$\text{Fe}^{3+}/\text{T.Fe}/\text{wt}\%$	$\text{Fe}^{2+}/\text{T.Fe}/\text{wt}\%$		$\text{Fe}^{3+}/\text{T.Fe}/\text{wt}\%$	$\text{Fe}^{2+}/\text{T.Fe}/\text{wt}\%$
1 000	50	1#	80.2	19.8	a	0	100
	20	2#	87.4	12.6	b	0	100
	10	3#	92.5	7.5	c	66.7	33.3
	5	4#	92.3	7.7	d	66.7	33.3
800	5	5#	70.3	29.7	e	66.7	33.3
900		6#	81.7	18.3	f	66.7	33.3
1 000		4#	92.3	7.7	d	66.7	33.3
1 100		7#	96.1	3.9	g	66.7	33.3

On the other hand, FeO was stable under N₂ atmosphere or a relatively higher CO/(CO+CO₂) atmosphere, and the diffractions peaks were found in Figs. 10 and 7 (Sample 1# and 2#).

In a word, the reaction mechanism between CaO and Fe₃O₄ under CO–CO₂ atmosphere can be regarded as multi-step reactions, Eqs. (1) and (2), and the total equation could be expressed as Eq. (3). CaO was regarded as a stabilizer for ferric oxide, which promoted the formation of Ca₂Fe₂O₅ and the oxidation of Fe₃O₄ to Fe₂O₃ under CO–CO₂ atmosphere.

4. Conclusions

The reaction between CaO and iron oxide under 2–50 vol% CO/(CO+CO₂) content at 800°C–1100°C were determined in the present work. The results indicated that Ca₂Fe₂O₅ could be easily when CaO and Fe₃O₄ were roasted under CO–CO₂ atmosphere, and the formation of Ca₂Fe₂O₅ was promoted by increasing the roasting temperature. Under this situation, CO₂ component in the CO–CO₂ atmosphere acts as an oxidative medium for the oxidation reaction of Fe²⁺ to Fe³⁺, and the oxidation process will be promoted by the formation of Ca₂Fe₂O₅. The reaction between CaO and Fe₃O₄ is regarded as multi-step reactions of 2CaO + Fe₃O₄ = Ca₂Fe₂O₅ + FeO and 3FeO + CO₂ = Fe₃O₄ + CO, and the total reaction is summarized as 6CaO + 2Fe₃O₄ + CO₂ = 3Ca₂Fe₂O₅ + CO.

Acknowledgements

The authors would express their heartfelt thanks to National Natural Science Foundation of China (No. 51574283 and No. 51234008), the Natural Science Foundation of Hunan Province, China (No. 2016JJ2143), Co-Innovation Center for Clean and Efficient Utilization of Strategic Metal Mineral Resources, and Hunan Provincial Innovation Foundation for Postgraduate (CX2015B054).

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