

Solid State Reduction of Preoxidized Chromite-iron Ore Pellets by Coal

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A comparative study on coal-based solid state reduction of preoxidized chromite pellets and chromite-iron ore pellets was conducted to investigate the reduction behavior of these two types of pellets. And the enhancement mechanism of chromite reduction reactions due to the pre-oxidation process of chromite with magnetite was revealed by means of optical microscopy, SEM with EDS. The results show the presence of iron ore and pre-oxidation process both are advantageous to the reduction of chromite. Pre-oxidation of chromite and iron ore mixture at 1323 K for 15 min contributes to more formation of sesquioxide solid solution (Fe, Cr, Al)₂O₃ than pure chromite oxidation. Massive cations exchange and diffusion occur between chromite and iron ore, which normally cause the decrease of magnesium content and aluminum content and the increase of iron content in spinel solid solution. Accordingly, the chromite reduction is enhanced with the metallization rate of chromite raised from 20.83% in prerduced chromite pellets to 47.98% in prerduced composite pellets at temperature of 1473 K for 90 min and C/O ratio=1.06, but no further improvement is observed above 1473 K. The mechanism study based on carbothermic reduction thermodynamics and the microstructure of prerduced pellets reveals the reduction of sesquioxide solid solution (Fe, Cr, Al)₂O₃ is more thermodynamically supported and the high iron, low magnesium and aluminum spinel solid solution formed in pre-oxidation process is also favorable for chromite reduction because of lower outward diffusion resistance of Fe²⁺ to the interface with CO gas.

KEY WORDS: coal-based reduction; preoxidized; chromite; chromite-iron ore pellets.

1. Introduction

Chromite ore is an essential raw material in producing ferrochromium alloys. At present, almost all of the ferrochromium alloys production is operated by means of the electric furnace smelting process, which generally applies high grade chromite ore as its feed material.^{1,2)} However, a decreasing availability of traditional lumpy ore for smelting as well as an increasing expense of chromite ore with high Cr₂O₃/FeO ratio that makes the stainless steel products less competitive in price. Therefore, utilization of relatively cost-effective chromite fines and concentrates, especially for that with low Cr₂O₃/FeO ratio, would be a trend in order to promote competitive advantage of the stainless steel products in the market.³⁾

China had successfully produced low-cost stainless steel master alloys with chromium content reaching 5%–21.3% by smelting reduction in Blast furnace (BF), which exhibits great advantages in using chromite fines and concentrates with low Cr₂O₃/FeO ratio.⁴⁾ Generally, chromite fines and concentrates are agglomerated in the form of pellets or sinter for their controllable chemical composition and better metallurgical properties before subsequent pyrometallurgical process. And the prerduced pellets are proved better

than traditional “lumpy ore” because they can contribute to lower energy consumption in furnace and better metallurgical properties.^{5–7)} However, chromite ores have extremely high soften-melting temperature, normally more than 1823 K (increases with the total content of MgO and Al₂O₃), which may make BF operations difficult.^{2,7)} Therefore, in order to reduce the melting point of the burden, a mixture of chromite concentrate and iron ore is utilized as feed material to produce prerduced pellets and the coal-based direct reduction process is widely adopted because China is seriously short of natural gas resources but has vast indigenous reserves of reducing coal.⁸⁾

The previous researches are mainly focused on solid state reduction of chromite ores or pre-oxidized chromite ores with high chromium grade. Radomysel'skii *et al.*⁹⁾ studied the coreduction of mixed iron and chromium oxides by hydrogen. It was found the reduction process could be enhanced because of the formation of a rhombohedral solid solution (Fe, Cr)₂O₃ in the pre-oxidation process. The same conclusion was drawn by Zhao and Hayes¹⁰⁾ based on a series of experiments to determine the effects of pre-oxidation of chromite pellets on the rates and extent of reduction in carbon monoxide gas. But it was also observed that the reduction rates above 1473 K would not be influenced by pre-oxidation because the sesquioxide solid solution (Fe, Cr)₂O₃ was rapidly reduced to chromite spinel FeCr₂O₄. Kapure *et al.*¹¹⁾ investigated the reduction of pre-oxidized

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chromite pellets at high temperature (1773 K) by coal reductant and concluded that pre-oxidization could improve the degree of iron and chromium metallization during reduction process. It was attributed to the formation of sesquioxide solid solution and generation of cation vacancies during the pre-oxidized process, both of which increased the reactivity of raw chromite and accelerated subsequent reduction process. Kherdr¹²⁾ studied the isothermal reduction of pre-oxidized Fe₂O₃-1–10% Cr₂O₃ mixture by Hydrogen at 1173–1473 K and found the doped Cr₂O₃ contributes to the formation of 18–26% (Fe, Cr)₂O₃ during the oxidation process, however, the sesquioxide (Fe, Cr)₂O₃ was less reducible than pure Fe₂O₃ and so pulled down the reduction extent from 100% to nearly 75% with increasing Cr₂O₃ at 1473 K for 30 min. On the other hand, reduction mechanism and kinetics of chromite ores were investigated by several researchers. Nafziger *et al.*¹³⁾ found the high iron chromite was more easily reduced and inferred the reduction process might be nucleation controlled because metal beads preferentially formed along cracks or at sites of imperfections. Chakraborty¹⁴⁾ studied the carbothermic reduction of chromite ores and found the reduction of iron and that of chromium were controlled by diffusion and chemical reactions or nucleation, respectively. And Perry *et al.*¹⁵⁾ developed an ionic diffusion model for chromite reduction and four stages of reduction were identified. The model can provide satisfactory explanations for the reduction mechanism of natural chromite ores or chromite pellets.^{10,16)} However, it lacks detail investigation on coal-based solid state reduction of pre-oxidized chromite-iron ore composite pellets, and it is also poorly understood the reduction behaviors of chromite-iron ore pellets were different from that of chromite pellets.

The present investigation is to reveal the reduction behaviors of pre-oxidized chromite-iron ore pellets by coal. The effects of reduction parameters (temperature, time and dosage of reducing agent) on solid reduction of chromite bearing pellets are researched and the reduction mechanism of chromite-iron ore pellets was explained based on the discussion of carbothermic reduction thermodynamics. Moreover,

the microstructures of the preoxidized pellets and pre-reduced pellets were also demonstrated.

2. Experimental Procedure

2.1. Raw Materials

One imported chromite concentrate from South Africa and a kind of domestic magnetite concentrate were used in the research. The bentonite clay was used as a binder to improve ballability of concentrates. The chromite concentrate has a narrow size distribution, mainly between 75 μ m and 125 μ m, accounting for almost 81.5%. The fineness of magnetite concentrate is 81.0% below 75 μ m.

The chemistry of the concentrates and bentonite is given in **Table 1**. The chromite concentrate contains 22.61% total Fe, 42.55% Cr₂O₃, 22.25% (MgO+Al₂O₃) and its Cr₂O₃/FeO ratio only reaches 1.99. It also has low content of impurities like silicon, phosphorus and sulfur, which is advantageous for blast furnace smelting process. For magnetite concentrate, it bears higher iron grade up to 65.12%, FeO content reaches 27.67% and low content of impurities except for its sulfur content reaching 0.19%. Bentonite is hydrous aluminosilicate that mainly composed of montmorillonite clay mineral assaying 72.40%, and the total content of alkali metal oxides is about 4.56%. The dosage of bentonite should be minimized in the prerequisite to meet the ball index.

The proximate analysis results of reducing agent and chemical composition of its ash are listed in **Table 2**. It can be found that the bituminous coal adopted in the research bears 52.12% fixed carbon content, low ash content of 4.49% and proper volatiles content of 30.41%. Proper content of volatile matter can contribute to the heat transfer and the reasonable temperature distribution in the reaction zone. Generally, in order to obtain excellent reduction conditions, reductant that with fixed carbon content over 50%, ash content lower than 20% and volatiles content ranging from 26% to 32% is appropriate for reduction.⁸⁾ From this point, the bituminous coal is good reductant.

Table 1. Chemical composition of concentrates and bentonite used in the research.

Sample	Mass fraction, %										LOI
	Fe _{Total}	FeO	Cr ₂ O ₃	CaO	MgO	Al ₂ O ₃	SiO ₂	(K ₂ O+Na ₂ O)	P	S	
C	22.61	21.38	42.55	1.86	8.82	13.43	1.88	–	0.0056	0.047	1.03
M	65.12	27.67	–	0.98	1.49	1.42	3.61	–	0.0210	0.190	0.99
B	1.28	Trace	–	4.17	0.23	14.20	62.12	4.56	0.0270	0.100	7.42

Note: C—chromite concentrate; M—magnetite concentrate; B—bentonite; LOI—Loss on ignition.

Table 2. Proximate analysis of reducing agent and chemical composition of its ash (wt, %).

Sample	Proximate analysis of coal				Chemical composition of ash					
	F _{cad}	M _{ad}	A _d	V _{daf}	Fe ₂ O ₃	CaO	MgO	Al ₂ O ₃	SiO ₂	S _{Total}
Coal	52.12	12.98	4.49	30.41	0.757	1.12	0.06	0.36	1.24	0.34

Note: F_{cad}—Fixed carbon content on air dried sample basis; M_{ad}—Moisture on air dried sample basis; A_d—Ash content on air dried sample basis; V_{daf}—Volatile matter determined on dried sample basis; S_{Total}—Total content of sulfur on dried sample basis.

2.2. Experimental Methods

In order to improve the ballability of chromite concentrate, it was pretreated in a wet ball mill ($\Phi 460 \times 620$ mm) before it was blended and mixed with magnetite concentrate. The fineness of pretreated chromite concentrate is 92.0% below 0.074 mm.

A mixture made from pretreated chromite concentrate and magnetite concentrate with the mass ratio of chromite to magnetite fixed at 2:3 (dry weight) along with dried bentonite (on ore basis) were blended and mixed manually as pellet feed. Then the feed and water was gradually added to a disc pelletizer with 1 000 mm in diameter and 15 mm rim

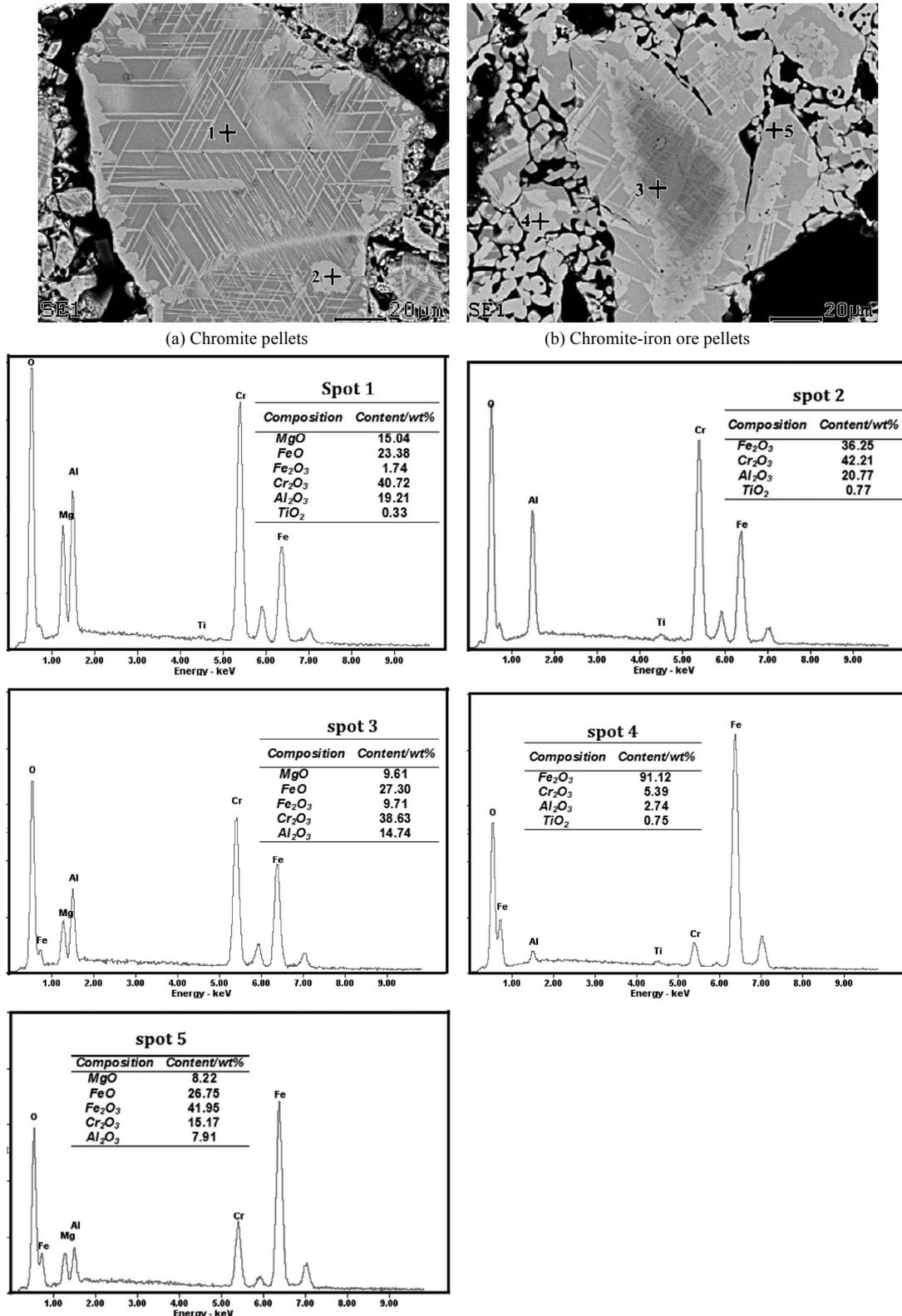


Fig. 1. SEM images of preoxidized pellets with EDS. Energy spectrum areas are: chromite spinel matrix (spot 1) and sesquioxide solid solution M₂O₃ (spot 2) in preoxidized chromite pellet (a); chromite spinel matrix (spot 3), Fe-rich sesquioxide solid solution (spot 4) and transition zone (spot 5) in the composite pellet (b).

depth, rotational speed at 28 r/min and inclined at 47° to the horizon. In 12 minutes' balling duration, about 3 kg qualified chromite-iron ore green pellets were produced with the moisture of 9.5% and diameter ranging from 10 mm–12.5 mm by screening for each batch. As a contrast, green pellets made from chromite concentrate only and dried bentonite (on ore basis) were prepared as well. Green pellets were required to have more than 4 times' drop on a steel plate from a height of 500 mm. Finally the green balls were dried in drying oven at 378 K for at least 4 hours until the molecular water was removed.

In every single factor experiment, 200 g dried Chromite-iron ore pellets or chromite pellets were loaded in a 300 ml corundum crucible and pre-oxidized in a muffle furnace under the condition of 1323 K for 15 min. Then hot pellets were taken out of the corundum crucible for a little while before two thirds of designed total proportion by weight of coal (broken to below 3 mm) were loaded into the hot crucible in advance, then the hot pellets were reloaded back and covered by the rest of coal, finally the corundum crucible was placed in another muffle furnace to complete reduction process under the condition of designed reduction temperature and time. After completing reduction process, the pre-reduced pellets were taken out and cooled in nitrogen. Reduction parameters including reduction temperature, reduction duration and adding proportion of coal were investigated.

The adding proportion of coal was expressed by C/O ratio, which was defined as the ratio of stoichiometric amount of fixed carbon to the total oxygen combined with Fe and Cr, calculated by Eq. (1). It was assumed that all iron and chromium were in the form of Fe₂O₃ and Cr₂O₃.

$$C/O \text{ ratio} = \frac{\text{The content of fixed carbon added in the reactor} \dots (1)}{\text{Total oxygen combined with Fe and Cr}}$$

And pre-reduced pellets were evaluated by metallization rate of iron phase determined from Eq. (2):

$$\eta_{Fe} = (M_{Fe} / T_{Fe}) \times 100\% \dots (2)$$

where η_{Fe} is the metallization rate based on iron phase, M_{Fe} and T_{Fe} that were determined by chemical titration methods represent metallic iron content and total iron content in the pre-reduced pellets.

Thermodynamics concerning reduction of chromite and iron ore was carried out to demonstrate reduction behaviors of chromite-iron ore composite pellets and the microstructures of preoxidized and pre-reduced were performed by Leica DMLP optical microscopy, FEI Quata-200 scanning electron microscope and EDAX32 genesis spectrometer.

3. Results and Discussion

3.1. Characteristics of Preoxidized Pellets

The microstructures of preoxidized pellets performed by SEM images with EDS were given in Fig. 1. It is noticeable that the Widmanstätten intergrowth of sesquioxide M₂O₃ (In general, M represents a serial of trivalent ions such as Fe³⁺, Cr³⁺ and Al³⁺.) within the grains and around the rims appears abundantly in both chromite pellets and chromite-iron ore pellets after the pre-oxidation process. The precipitated maghemite-type sesquioxide M₂O₃ is a coherent

metastable intermediate phase which is achieved by changing an ABC packing into ABAB packing by the dislocations gliding along (111) plane of spinel.¹⁷⁾ Particles remain relatively independent with less particle-particle interactions in chromite pellet (Fig. 1(a)) while effective interactions occur between chromite and iron ore with more formation of sesquioxide (Fe, Cr, Al)₂O₃ in the composite pellet (Fig. 1(b)). According to energy spectrum analysis (Fig. 1, spot 1, 3, 5), there exists cations concentrate gradients from chromite to iron ore and it can be inferred diffusion of cations like Mg²⁺, Al³⁺, Ti⁴⁺ and Cr³⁺ can happen when chromite is close to iron ore.

During the pre-oxidation process, as can be seen from Table 3, most Fe²⁺ ions are oxidized to Fe³⁺ ions in both chromite pellet and composite pellet with FeO contents assayed 4.88% and 2.85%, respectively. A lot of cation vacancies as (Fe³⁺)_{1-x}[Fe³⁺□]_xO₄ generate when Fe₃O₄ is oxidized to maghemite-type phase γ-Fe₂O₃, which attracts Mg²⁺, Al³⁺ ions' diffusion from chromite spinel to nearby iron ore particle and counter-diffusion of Fe²⁺, Fe³⁺ ions to chromite spinels. The cations exchanges contribute to the obvious size reduction of chromite spinel particles and enlargement of connecting neck between chromite spinel and iron ore particles. Moreover, effective diffusion of cations causes the decrease of magnesium content and aluminum content and the increase of iron content in spinel solid solution.

3.2. Reduction Test of Preoxidized Pellets

Effects of reduction temperature, C/O ratio and reduction time on metallization rate (iron phase) of chromite-iron ore pellets and chromite pellets are shown in Figs. 2, 3 and 4, respectively.

Table 3. The chemical composition of preoxidized pellets (wt, %).

	Fe _{Total}	FeO	Cr ₂ O ₃	CaO	MgO	Al ₂ O ₃	SiO ₂
Chromite pellets	22.60	4.88	42.52	1.91	8.82	13.59	2.62
Chromite-iron ore pellets	48.06	2.85	16.99	1.38	4.42	6.39	3.69

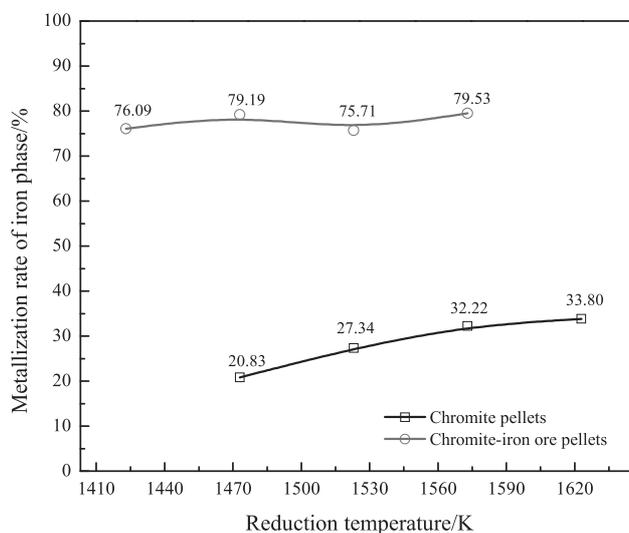


Fig. 2. Effects of reduction temperature on metallization rate of pre-reduced pellets. For both chromite pellets and chromite-iron ore pellets, reduction time was fixed at 90 min with C/O ratio fixed at 1.06.

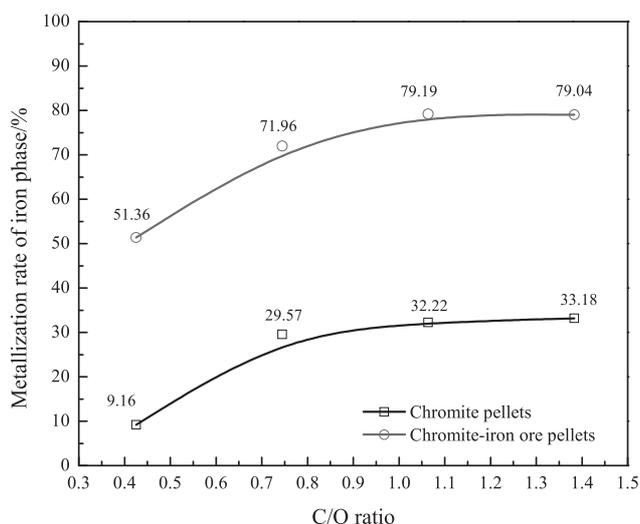


Fig. 3. Effects of C/O ratio on metallization rate of prerduced pellets. For chromite pellets, reduction temperature was fixed at 1 573 K with a duration of 90 min while for chromite-iron ore pellets, reduction temperature was fixed at 1 473 K with a duration of 90 min.

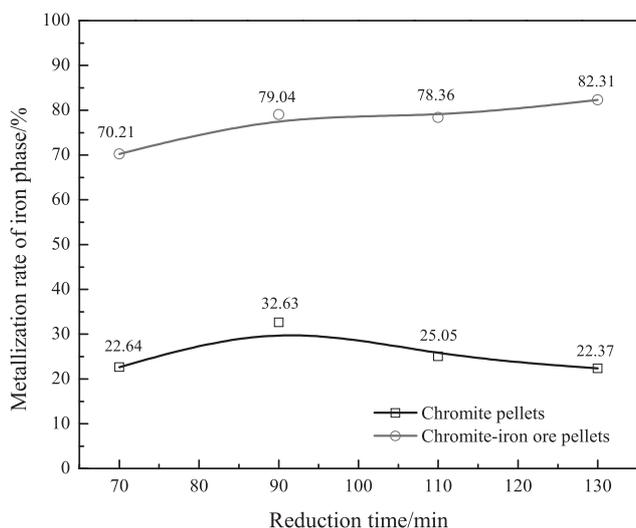


Fig. 4. Effects of reduction time on metallization rate of prerduced pellets. For chromite pellets, reduction temperature was fixed at 1 573 K with C/O ratio of 1.06 while for chromite-iron ore pellets reduction temperature was fixed at 1 473 K with C/O ratio of 1.38.

As is depicted in Fig. 2, the metallization rate of chromite-iron ore pellets reaches 79.19% at 1 473 K and remains relatively steady when reduction temperature varies from 1 423 K to 1 573 K, however, the metallization rate of chromite pellets can only achieve 33.8% even at a higher temperature of 1 623 K.

The reduction of both chromite and iron ore is heavily dependent on the carbon monoxide partial pressure in the reactor. More coal addition means stronger reducing atmosphere (higher carbon partial pressure) and longer maintenance time, in other words, the prerduced pellets are less likely to be re-oxidized. Therefore, the metallization rates of both chromite-iron pellets and chromite pellets change dramatically when changing C/O ratio from 0.42 to 1.06 (Fig. 3). For chromite-iron pellets, its metallization rate increases

from 51.36% to 79.19%, while for chromite pellets, the metallization rate exhibits a relatively slow increase from 9.16% to 33.18%. However, no significant change of both metallization rates of pellets is observed when the C/O ratio increases from 1.06 to 1.38. It can be revealed from Figs. 2 and 3 that the reduction conditions (1 423 K to 1 573 K for 90 min, C/O ratio=1.06) are good enough for the reduction of iron oxides and sesquioxide. Accordingly, the stable metallization rate of chromite-iron ore pellets at 1 423 K to 1 573 K may be attributed to the internal diffusion of CO gas into the chromite-iron ore pellet, which becomes the rate-controlling step at the temperature range of 1 423 K to 1 573 K. As a result, the reduction of chromite spinel solid solution is hindered.

The reduction of chromite pellets usually needed long reduction duration in order to gain high metallization rate because of poor reducibility of iron phase and chromium phase in chromite spinel. As is demonstrated in Fig. 4, with the increasing reduction time from 70 min to 130 min, metallization rate of chromite-iron ore pellets rise from 70.21% to a maximum value of 82.31%. For chromite pellets, a maximum metallization rate of 32.63% is achieved at reduction duration of 90 min, and then gradually decreases to 22.37% when reduced for 130 min. The different behaviors of two metallization rates can be attributed to the differences of reduction temperature and C/O ratios between chromite-iron ore pellet and chromite pellet. For chromite-iron ore pellet, the C/O ratio is 1.38 and it is enough for the whole reduction duration (130 min) at 1 473 K, therefore, its metallization rate keeps rising with the increasing reduction. However, for chromite pellet, the C/O ratio was fixed at 1.06 and the reduction temperature is 1 573 K. It means the gasification of the coal is much quicker and the coal addition is not enough for longer reduction duration. As a result, the metallic phases may be re-oxidized and the metallization rate decreases.

On the basis of reduction test, assuming all iron in iron ore were reduced to metallic iron in prerduced pellets, then the corresponding contributions to metallization rate made by reduction of iron ore and chromite were calculated and listed in Table 4. It shows that the presence of iron ore can significantly contribute to the reduction of iron in chromite. The metallization rate of chromite in prerduced pellets increases markedly from 20.83% to 47.98% at reduction temperature of 1 473 K for 90 min, C/O ratio=1.06. This percentage may be higher because it is difficult to reduce all iron in iron ore to metallic iron in a limited time.⁸⁾ However, the strengthen effect on the reduction of chromite gets weak when the reduction temperature reaches 1 573 K. The metallization rate of chromite remains almost stable from 1 473 K to 1 573 K. This is in consistence with the explanation of increasing internal diffusion resistance of CO gas that makes the further reduction of chromite spinel solid solutions more difficult. The increasing internal diffusion resistance of CO gas may result from a dense layer (shell) formed by quick metalized irons on the outer surface of pellets in which the internal diffusion channel of CO gas is blocked.¹⁸⁾ Another explanation is that the porosity of the pellets may decrease because the growth and efficient connections of metallic irons, and as a result, it hinders the internal diffusion of CO gas.¹⁹⁾

Table 4. Effects of iron ore on reduction of iron phase in chromite.

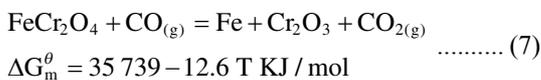
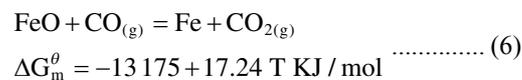
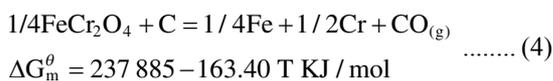
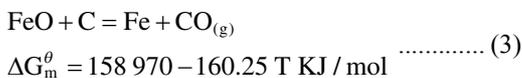
	Mass fraction, %					
	Fe _{Total}	M _{Fe}	η _{Fe}	M _{Fe-iron ore}	M _{Fe-chromite}	η _{Fe-chromite}
Prereduced chromite pellets						
a. reduction temp. 1 473 K	24.00	5.00	20.83	–	5.00	20.83
b. reduction temp. 1 573 K	24.02	7.74	32.22	–	7.74	32.22
Prereduced chromite-iron ore pellets						
a. reduction temp. 1 473 K	56.22	44.52	79.19	33.73	10.79	47.98
b. reduction temp. 1 573 K	56.22	44.71	79.53	33.73	10.98	48.82

Note: 1. Reduction is conducted under the same C/O ratio and reduction duration; 2. M_{Fe-iron ore} is a theoretical value of metallic iron grade contributed by reduction of iron ore; M_{Fe-chromite} represents metallic iron grade contributed by reduction of chromite and it was determined by: M_{Fe-chromite} = M_{Fe-iron ore} × η_{Fe-chromite}; η_{Fe-chromite} is a theoretical metallization rate contributed by reduction of chromite.

3.3. Enhancement Mechanism of Chromite Reduction in Prereduced Composite Pellets

In order to reveal the enhancement mechanism of chromite reduction in prereduced composite pellets due to the pre-oxidation with magnetite, the microstructure of both prereduced chromite pellets and chromite-iron ore pellets obtained under the same conditions (reduced at 1 473 K for 90 min and C/O ratio is 1.06) were investigated and demonstrated by means of optical microscopy, SEM and energy spectrum analysis.

Generally, reduction of iron phase in iron ore has a priority over reduction of iron phase in chromite.¹⁴⁾ When reduced by coal, the rate-controlled reactions in pellets are presented in Eqs. (3)–(7),^{8,18)} respectively.



Considering effects of equilibrium vapor composition on reactions (3–7), the equilibrium diagram of carbon reduction is given in Fig. 5. And it can be inferred that for reduction of chromite reaction (3) starts from 1 456 K and reaction (7) starts from 1 301 K (point c), which are much higher than that of iron ore with starting reduction temperature of 992 K for reaction (3) and 1 031 K (point b) for reaction (6). Carbon monoxide reduction of iron in iron ore and chromite is also highly correlated with equilibrium vapor composition. As is shown in Fig. 5, over 93% of carbon monoxide concentrate is demanded for reduction of chromite, however, reduction of iron ore can happen when carbon monoxide concentrate is over 63%. Higher carbon monoxide concentrate in reducing gas means iron in chromite is more difficult

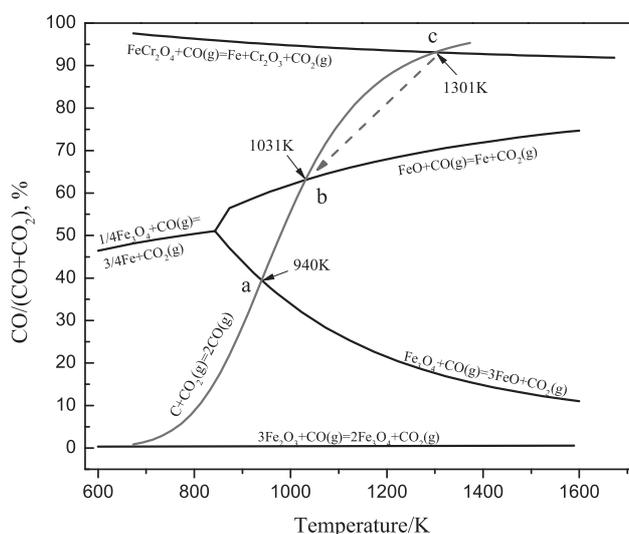
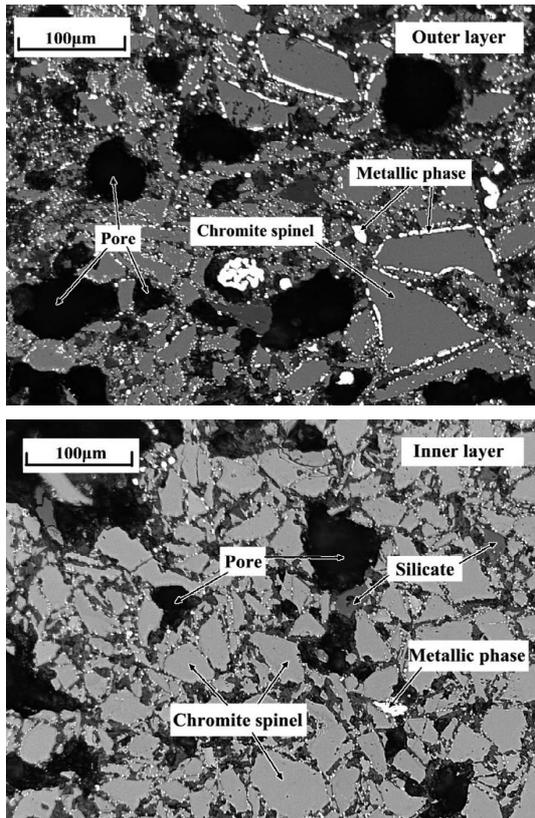


Fig. 5. Equilibrium diagram of reduction of chromite-iron pellets by carbon.

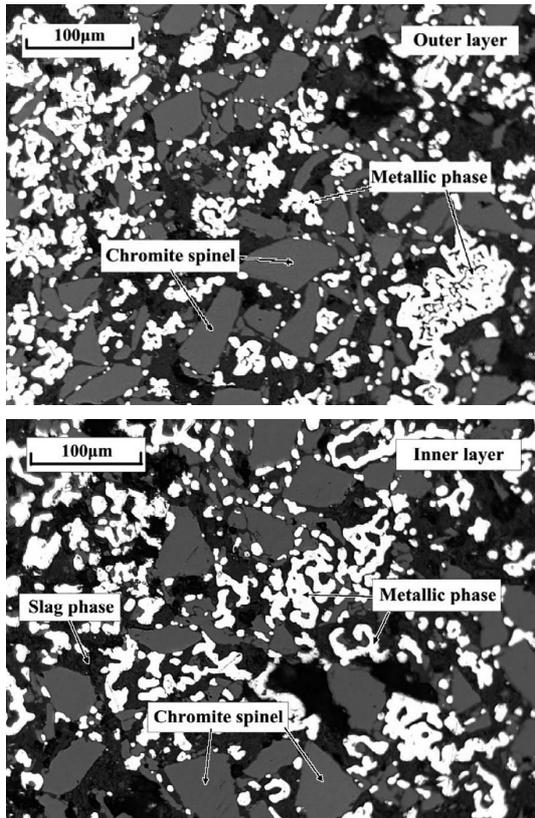
to be reduced and more consumption of carbon are needed to maintain strong reduction atmosphere.

For sesquioxide (Fe, Cr, Al)₂O₃, according to the previous researches,^{10,12)} its reducibility is better than chromite spinel (Fe, Mg)[Cr, Al, Fe]₂O₄ but inferior to iron oxide Fe₂O₃. Reducing tendency from point c to point b, as the dotted line shown in Fig. 5, represents reduction of (Fe, Cr, Al)₂O₃ is more thermodynamically supported than spinel solid solution. However, the less substitution of Mg²⁺, Al³⁺ ions for Fe²⁺, Fe³⁺ ions in spinel solid solution is favorable for reduction because Mg²⁺, Al³⁺ ions can stabilize thermodynamically the spinel solid solution making the reduction difficult.

Therefore, as is displayed in Fig. 6, there is much more metallic phase in prereduced chromite-iron ore pellets than that in chromite pellets. And metallic phase distributes in both outer layer and inner layer of chromite-iron ore pellets, however, fewer metallic phase can be found in inner layer of chromite pellets. It may attribute to insufficient CO equilibrium concentrate at interaction interface which cannot thermodynamically support the reduction of iron in chromite. Moreover, it can be obviously observed chromite-iron ore pellets have smaller chromite particle average size and larger particle-particle distance than that in chromite pellets.



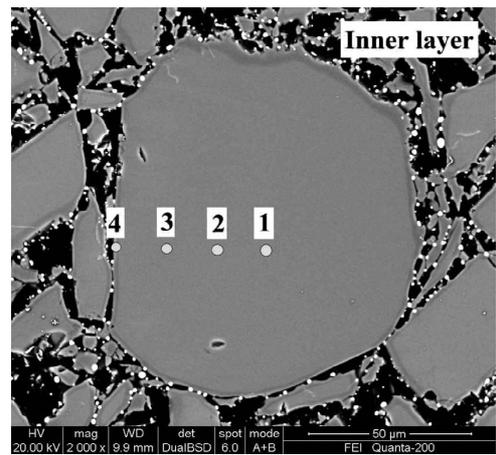
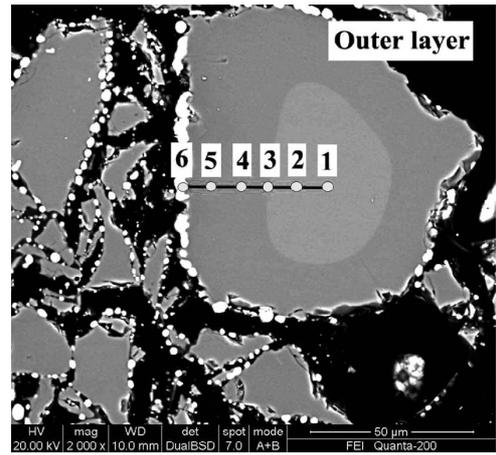
a. Prereduced chromite pellets



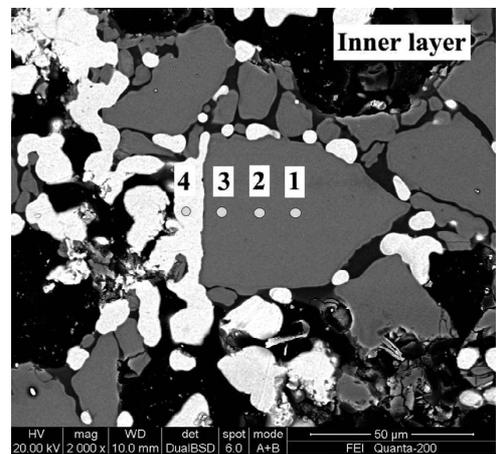
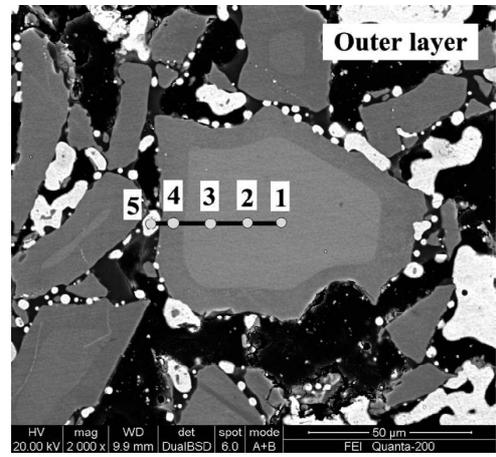
b. Prereduced chromite-iron ore pellets

Fig. 6. Microstructure of prereduced pellets.

Further examination (Fig. 7) by SEM show nucleation and growth of metallic phase in prereduced chromite pellets preferentially occur on the external surface of chromite particles, whereas that in prereduced chromite-iron ore pellets



(1) Prereduced chromite pellets



(2) Prereduced chromite-iron ore pellets

Fig. 7. SEM micrographs of prereduced pellets.

Table 5. Spot scan analysis of chromite particles in prereduced pellets.

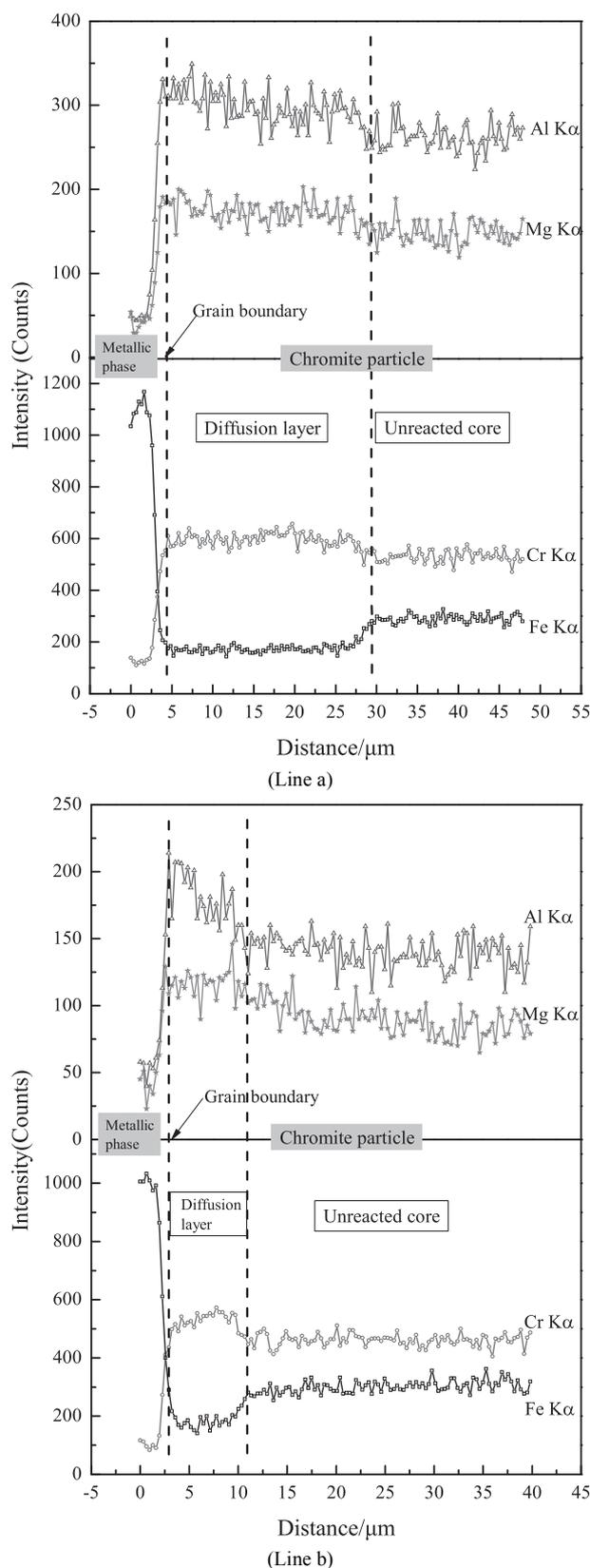
Points	Outer layer, wt/%					Inner layer, wt/%				
	Fe	Cr	Al	Mg	O	Fe	Cr	Al	Mg	O
(1) Prereduced chromite pellets										
1	28.03	36.20	12.59	7.12	14.47	26.03	33.58	14.64	7.05	17.23
2	27.90	36.13	12.51	7.13	14.49	25.97	33.94	14.56	6.98	17.08
3	17.91	42.66	14.00	8.37	15.21	26.12	33.85	14.60	7.02	17.20
4	16.14	44.14	14.09	8.26	15.48	19.78	36.06	16.48	8.01	18.23
5	15.38	42.63	15.29	9.53	15.51	–				
6	94.54	5.46	0.00	0.00	0.00					
(2) Prereduced chromite-iron ore pellets										
1	39.62	40.87	7.54	3.74	6.40	31.04	39.35	12.50	6.70	8.80
2	39.13	39.82	7.52	4.34	6.45	31.05	38.92	12.47	6.61	8.77
3	36.82	40.83	7.62	5.65	6.48	31.75	38.45	12.70	6.73	8.89
4	20.99	51.68	9.49	6.77	7.55	97.58	2.42	0.00	0.00	0.00
5	97.59	2.41	0.00	0.00	0.00	–				

may also happen on the surface of iron ore. Zhao and Hayes pointed out metallic phase virtually appeared to deposit at the sites where sesquioxide has previously formed and this preferential nucleation may result from the absence of MgO which would thermodynamically stabilize both iron phases and spinel.¹⁹⁾ It can be inferred the presence of iron ore provides a favorable dynamic conditions for the nucleation and growth of metallic iron.

Energy spectrum analysis and line-scan analysis of various points from metallic phase at external surface of chromite straight to the center of chromite particles in outer and inner regions indicates ionic diffusion occur during solid state reduction of chromite (Table 5 and Fig. 8-Line a/b). In outer layer of prereduced pellets, metallic phase concentrates on the external surface of chromite particle and Cr³⁺, Al³⁺, Mg²⁺ ions content slightly enrich in outer regions of chromite particles with an iron-enriched core formed in the center. A “bilayer structure” of chromite particle consisting of an unreacted core with relatively constant content of metal cations and a diffusion layer with diffusion concentration gradients of metal cations from surface of unreacted core to external surface of particles appears while contents of metal cations remain stable in inner layer of prereduced pellets.

When compared with chromite pellets, chromite particles in chromite-iron ore pellets have higher content of iron and chromium but lower content of magnesium, aluminum and oxygen. Lower oxygen content in prereduced chromite-iron ore pellets means preferential reduction of trivalent irons to divalent irons in sesquioxide solid solution (Fe, Cr, Al)₂O₃ rather than that in chromite spinel (Fe²⁺, Mg)[Cr, Al, Fe³⁺]₂O₄, and consequently causes greater mass loss of oxygen. It can also prove more sesquioxide solid solution forms in chromite-iron ore pellets.

In addition, as mentioned above, reduction of low magnesium and aluminum spinel is more easily. When Fe²⁺ is reduced to Fe⁰ on the surface of chromite spinel, competitive occupation between Fe²⁺ and Mg²⁺ ions in tetrahedral cation defects occur to maintain electrical neutrality. Since


Fig. 8. Line-scan analysis along line a and b.

both the increase of iron content and the decrease of magnesium content in chromite particles enable Fe²⁺ ions possess higher possibilities to occupy tetrahedral cation defects, thus reduce the outward diffusion resistance of Fe²⁺ ions to interface with CO gas and improve the reduction of chromite.

4. Conclusion

(1) Pre-oxidation of chromite and iron ore mixture at 1323 K for 15 min can not only improve the formation of sesquioxide solid solution (Fe, Cr, Al)₂O₃, but also contribute to cations exchange between iron ore and chromite. It brings composition redistribution of chromite particles, which normally leads to the decrease of magnesium content and aluminum content and the increase of iron content in chromite.

(2) The reduction of chromite can be enhanced by pre-oxidation at presence of iron ore. The metallization rate of chromite can be raised from 20.83% (chromite only) to 47.98% (coexistent of iron ore) at 1473 K for 90 min and C/O ratio=1.06. However, no further obvious improvement is observed above 1473 K in composite pellets because the internal diffusion of CO gas may become the rate-controlling step at this temperature range and such hinders the further reduction of chromite spinel solid solution.

(3) The enhancement mechanisms of chromite reduction by pre-oxidation with iron ore reveal the reduction of sesquioxide solid solution (Fe, Cr, Al)₂O₃ is more thermodynamically supported. And another common phase-the high iron, low magnesium and aluminum spinel solid solution formed in the pre-oxidation process is also favorable for chromite reduction because it has lower outward diffusion resistance for Fe²⁺ ions from iron-enriched core of chromite particles to the interface with CO gas.

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