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EFFECTS OF CaO, MgO, Al_2O_3 AND SiO_2 ON THE CARBOTHERMIC REDUCTION OF SYNTHETIC $FeCr_2O_4$

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Abstract

In order to optimize the current reduction process of chromite, a good knowledge of reduction mechanism involved is required. The basic component in chromite ore is $FeCr_2O_4$ with gangue component like MgO and Al_2O_3. In lack of clear and consistent explanation about the effect of addition on the reduction of $FeCr_2O_4$, investigation of synthetic $FeCr_2O_4$ with different kind and amount of additions was carried out at 1673K under isothermal mode. Kinetic mechanism was also studied by linear fitting of different kinetic equations. Combined with rate-controlling step, it could be concluded as follows. CaO could enhance the reduction because Ca^{2+} would replace Fe^{2+}, thus facilitated the ion diffusion in solid phase. Al_2O_3 had a positive influence as well, since Al^{3+} could form a solid solution phase with Cr^{3+} and made Cr^{3+} reduced more easily. MgO would hinder the reduction due to formation of a more stable phase $MgCr_2O_4$. SiO_2 would also hamper the Cr metallization because there was a liquid phase formed when Cr^{3+} was reduced to divalent, which would impede the nucleation of reduction product.

***Key words**: synthetic chromite, addition, kinetics, carbothermic reduction*

1. Introduction

Chromite is the main material for the production of ferroalloy and stainless steel. Nowadays, in order to gain a higher reduction degree and lower the energy consumption [1], direct alloying of some elements, such as chromium, is under discussion. However, because of the refractory property of the ores and the very fast steel making, direct alloying can be very difficult to achieve in such a short time. For a better understanding of reduction behavior of chromite, investigations were carried out focusing both on the solid-state reduction and on the smelting reduction.

Chromite ore has a main composition of $FeCr_2O_4$ and main gangue of MgO and Al_2O_3. As to the solid-state reduction, investigators [2-8] reported varied factors that affected the reduction behavior, mainly including temperature, properties of chromite and reducing agent etc. Moreover, Perry et al. [9] and Soykan et al. [10] proposed the ion diffusion mechanism for reduction process while Lekatou et al. [11] gave a relatively clear description of the reaction steps. Different kinetics models were also employed to discuss the rate-controlling steps.

It is worth mentioning the interest to the additional fluxes from researchers. Since the main compositions of gangue are MgO and Al_2O_3, which combine as spinel and thus are difficult to smelt. So researchers [12-17] employed SiO_2 to form compound with low melting point, and in this way liquid slag can be formed and thus Cr could be reduced in the slag and reduction process was enhanced. But Lekatou [15] also mentioned that besides its positive effect, too much amount of SiO_2 might hinder the contact of chromite and carbon. Therefore, the account of SiO_2 had a critical value, which was greatly related to the carbon content and the MgO/Al_2O_3 ratio in the chromite. This finding agreed much with that of Ding [16]. Ding [18] also investigated the effect of lime. At the early stage of reduction, with increasing lime amount, the apparent activation energy presented a decreasing trend, which suggested that CaO could act as a catalytic agent. But the catalytical mechanism was not clear enough. Neuschutz [19] studied complex additives and reported they affected the reactions by facilitating the nucleation to form $CaO{\cdot}MgO{\cdot}Al_2O_3$ particles or accelerating the diffusion of Cr by forming liquid slag. Katayama et al. [20] found that addition of alkali metal slats such as NaCl leaded to improved reduction rate at moderate

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temperature by increasing the rate of Boudouard reaction. Li et al. [21] reported that alkali metal salts could increase the rate of reduction but without giving a clear mechanism. Van Deventer [22] studied the effect of SiO_2, Al_2O_3, K_2CO_3, Na_2O_2, CaO, MgO, Fe and Cr and discovered that they all affected Boudouard reaction positively. However, MgO and Al_2O_3 would inhibit carbothermic reduction, and olivine and carbide were both identified as products. However, Dawson et al. [23] implied that the Boudouard reaction was rate-limiting step only at moderate temperature, and at high temperature, alkali metal fluoride would form eutectic mixture and act as a solvent for spinel constituents.

In our previous study [24], the kinetics of solid reduction of $FeCr_2O_4$ has been analyzed; the iron metallic process is the nuclear controlling, while the chromium oxide reduction is limited in the solid diffusion step. However, the components of different kinds of chromite ore vary, thus necessitating a proper match for each kind of chromite. Furthermore, after the chromite particle break down and iron and chromium oxides are exposed, effect of gangue component on the reduction of pure $FeCr_2O_4$ is seldom reported. Meanwhile, as to the influencing mechanism, there has not been a consistent conclusion. The effect of different addition during each reduction period has not been discussed thoroughly. So it is worthwhile to study the reduction behavior of $FeCr_2O_4$ in different additives to provide an optimizing direction for slag composition optimization in smelting practice.

2. Experiment

Pellets were prepared by compaction of thoroughly mixed powder of analytical pure Fe and Fe_3O_4 in steel dies under a pressure of 12MPa. And the briquettes were held in an iron crucible and heated at 1373K for about 10 hours to form FeO. Then the compacted pellets of mixed FeO and Cr_2O_3 were treated under the same condition for 48 hours. X-ray diffraction pattern for the synthetic $FeCr_2O_4$ was shown in Fig. 1, which confirmed the product was pure enough for the conduction of reduction experiments.

Synthetic chromite prepared as above (-200mesh) was mixed with graphite powder (purity98.5 wt%) and the quantity of carbon was equal to the presumed value when the carbon is exactly reacted to form CO as equation (1).

$$FeCr_2O_4+4C \rightarrow Fe+2Cr+4CO \quad (1)$$

$CaCO_3$ powder (Sinopharm Chemical Reagent, AR) was calcined at 1373K for 6 hours to decompose any hydroxide and carbonate to form CaO. For SiO_2, MgO and Al_2O_3 (all Sinopharm Chemical Reagent, AR), these oxides were heated at 1273K for 4 hours to remove moisture and stored in a desiccator before use. The mole ratios of additives to $FeCr_2O_4$ were 2 and 4 respectively. Appropriate amount of materials were mixed and ground thoroughly in an agate mortar.

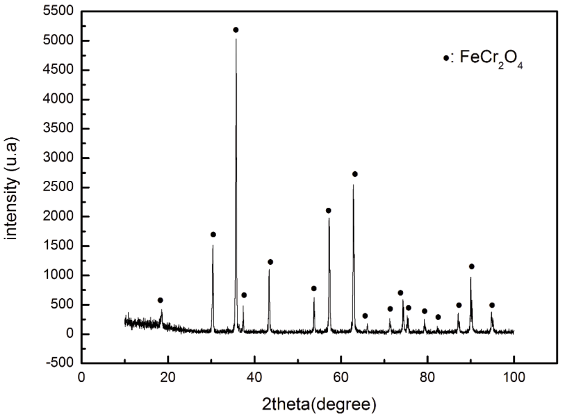


Figure 1. *X-ray diffraction pattern for the synthetic $FeCr_2O_4$*

Reduction of synthetic chromite was undertaken by isothermal methods at 1673K. Experiment was conducted in a molybdenum-wire furnace. A thermocouple (PtRh30-PrRh6) was used to monitor the experimental temperature. Argon gas with a flow rate of 300mL/min was introduced to the reaction tube in order to guarantee a non-oxidizing atmosphere. Alumina crucibles of a volume of 5 mL were employed to hold the powders and they were hung by molybdenum-wire and alumina tube with an ID of 6mm to a thermobalance with an accuracy of 0.001g, which could record the sample weight during the experiment. The alumina tube was used in the furnace because it was an open system and molybdenum-wire was likely to be oxidized at a pretty low oxygen partial pressure. The molybdenum-wire furnace was heated to the 1673K and precaution was taken to determine the length of the molybdenum-wire to insure that the crucibles were placed right in the even-temperature zone of the furnace, which was about 0.08 meters. After experiment, the sample was taken out of the furnace at once and treated with Argon gas to maintain the reduced state as exactly as possible.

Since reduction experiments were carried out at relatively high temperatures between 1473K-1673K in which carbon monoxide was more stable than carbon dioxide and the argon flow in high purity would take the gas product away continuously, the assumed gas product was CO when calculating the reduction degree. Hence the reduction fraction is given by equation (2).

$$R=\frac{\text{observed weight loss}\times 16/28}{\text{total removable oxygen}} \quad (2)$$

3. Results and discussion

3.1 Effect of CaO

The reduction calculated according to equation (2) as a function of time was plotted in Fig.2. As can be seen, during the initial period, adding additives slightly hindered the reduction of chromite. However, when the reduction degree reached about 30%, chromite with CaO was reduced more rapidly, and with increased CaO content, the final reduction degree increased from 80% to nearly 90%.

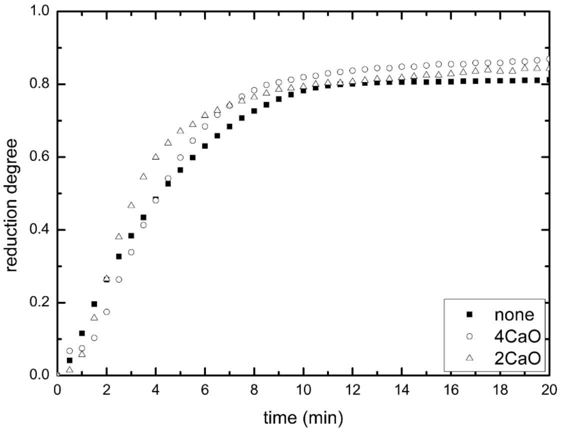


Figure 2. *Reduction degree as a function of time with CaO*

In order to examine the effect of CaO during the reduction process, samples with a CaO molar ratio equal to 2 which were reduced after 2min and 6min were examined by XRD. Fig. 3 gave the XRD patterns.

With the proceeding of experiment, the synthetic chromite decomposed gradually, forming chromium oxide and carbide, which indicated that chromite was reduced by two steps. This proposal was consistent with the previous study [23]. Although several studies have pointed out that CaO may enter the spinel lattice with the release of FeO component, the reduction degree of the initial stage is not observed improving in the current study compared with none addition case. Fig.3(a) also supports the above findings. Thus, another negative effect of CaO on the reduction is to confine the contact between chromite with reductant, which presents a diluting effect.

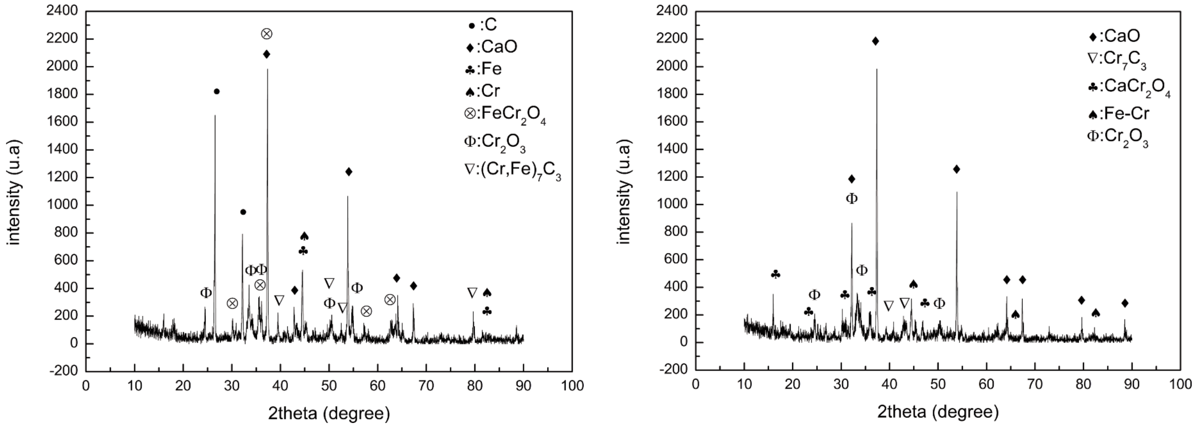
When chromite was reduced after 6min, a phase $CaCr_2O_4$ formed, and the corresponding reduction degree started to be higher than the blank case. This might indicate that the Cr^{3+} diffusion in the solid phase is facilitated by the formation of $CaCr_2O_4$, and also increasing the probability contacting with the carbon. In the view point of thermodynamics, the Standard Gibbs energy change of the $CaCr_2O_4$ reduction with carbon at 1673K is -662.1kJ/mol, which is higher than the value of the Cr_2O_3 reduction -960.3kJ/mol. Equation (3) and (4) present the formula and Standard Gibbs Energy. But the rate determining step of the Cr metallic process has been overcome to some extent, thus the reduction degree can be enhanced compared with none addition case.

$$7CaCr_2O_4 + 27C = 7CaO + 2Cr_7C_3 + 21CO,$$
$$\Delta G^{\theta}_{1673K} = -662.1kJ/mol \qquad (3)$$

$$7Cr_2O_3 + 27C = 2Cr_7C_3 + 21CO,$$
$$\Delta G^{\theta}_{1673K} = -960.3kJ/mol \qquad (4)$$

3.2 Effect of SiO_2

When the chromite was reduced with existence of SiO_2, the reduction degree as a function of time was plotted as Fig. 4. As was shown in Fig. 4, the influence of SiO_2 in the initial period was not obvious. When the reduction degree reached about 50%,



a. 2min *b. 6min*

Figure 3*. X-ray patterns of samples reduced after 2min and 6min*

chromite with SiO_2 seemed more difficult to reduce. But the same reduction degree with /without SiO_2 addition was achieved after 20min. This trend suggested that the SiO_2 delayed the reduction rate, mainly in the Cr metallic stage. And the increasing amount of SiO_2 can improve the reduction degree further, which is approaching the reduction level without SiO_2 addition.

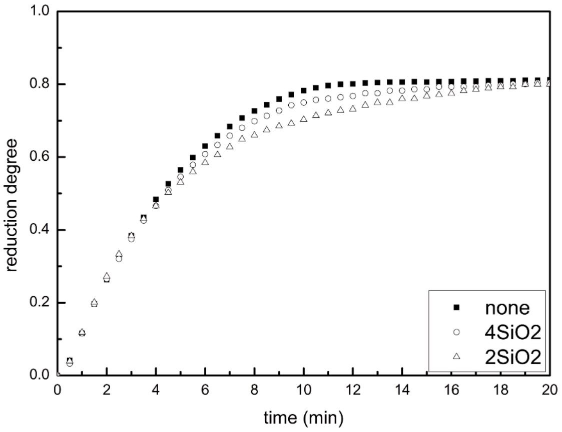


Figure 4. *Reduction degree as a function of time with* SiO_2

XRD patterns and SEM pictures of samples after experiment were shown in Fig.5-6. In the XRD patterns, besides the Fe-Cr alloy and additive SiO_2, remaining carbon and chromium oxide were also observed. It was sure that the reduction of chromite was not completed. In the XRD results, there was no new product observed. But in the SEM pictures, there appeared small amount of liquid phase formed in the course of reduction degree was higher than 65% It is known that the reduction of Cr_2O_3 also proceeded as $Cr^{3+}\rightarrow Cr^{2+}\rightarrow Cr$, similarly as the hematite. When the Cr_2O_3 reduced to CrO, which meant the reduction degree reached about 50%, SiO_2 would act as a solvent to allow the CrO to dissolve in. The phase diagram of SiO_2-CrO (Fig.7) also supported such deduction because there was a eutectic phase in a certain below 1673K. Therefore when Cr^{3+} was reduced to Cr^{2+}, CrO and SiO_2 were melted, thus hampered the reduction of Cr^{2+} to Cr due to the separation from the reductant.

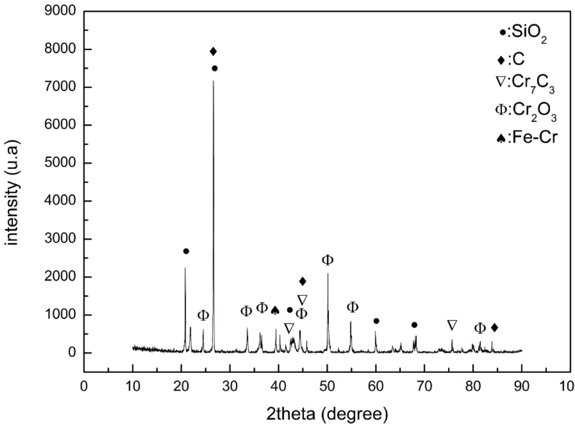


Figure 5. *X-ray patterns of samples reduced after 5min*

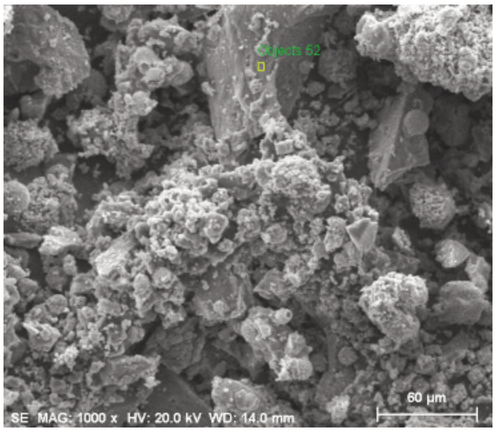


Figure 6. *SEM photo and EDS analysis of samples reduced after 6min*

Table 3. *EDS analysis of the marked point*

element	Atom ratio(%)
Si	43.4
O	45.59
Cr	11.01

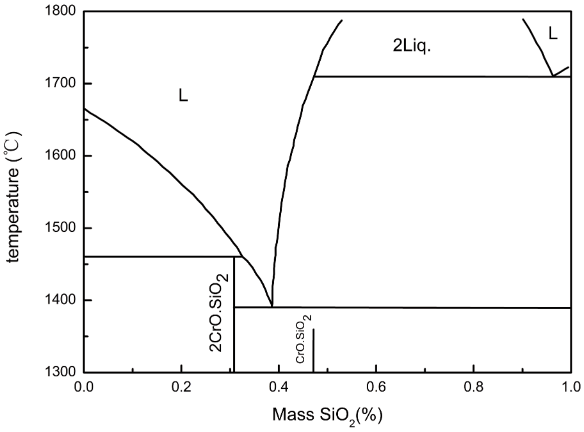


Figure 7. *Phase diagram of binary CrO-*SiO_2 [23]

3.3 Effect of MgO

Reduction behavior with existence of MgO was presented in Fig. 8. And XRD patterns and SEM pictures were shown in Fig. 9-10. In the initial period, the effect of MgO was slight but when the reduction degree reached about 65%, the rate dropped dramatically and the final reduction degree could not exceed 80% any more. In the XRD pattern, $MgCr_2O_4$ was observed. As mentioned in many previous works [9-10], $FeCr_2O_4$ was in a structure of spinel, associated with some $MgAl_2O_4$ because the Mg^{2+} and Fe^{2+} were located in the same position. So when MgO was present, Mg^{2+} and Cr^{3+} would form a more stable structure resulting that the reduction of chromite became difficult. Unlike the samples with CaO, when a surface scanning was taken, Mg coexisted with other elements like Fe and Cr. Therefore, it could be inferred that MgO as an additive ended in forming a new phase. Compared with $FeCr_2O_4$, $MgCr_2O_4$ is more stable and difficult to reduce based on Equation(5). Thus, it can be expected that much amount of MgO would postpone the proceeding of reduction.

$$7MgCr_2O_4 + 27C = 7MgO + 2Cr_7C_3 + 21CO,$$
$$\Delta G^{\theta}_{1673K} = -553.1 kJ/mol \qquad (5)$$

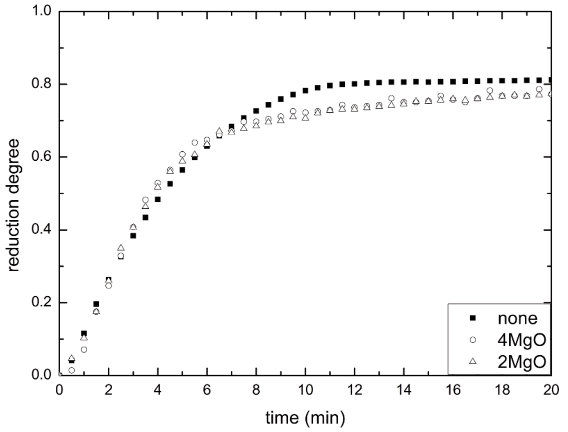
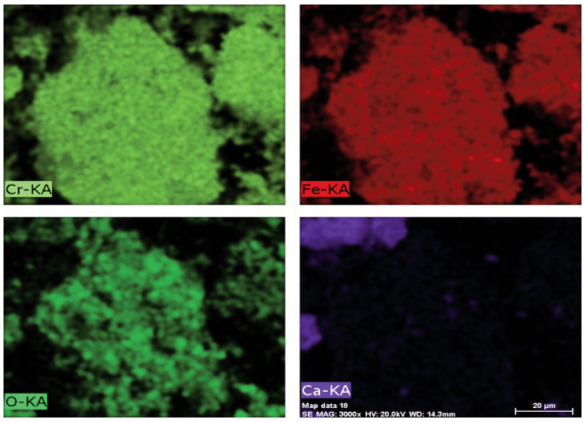
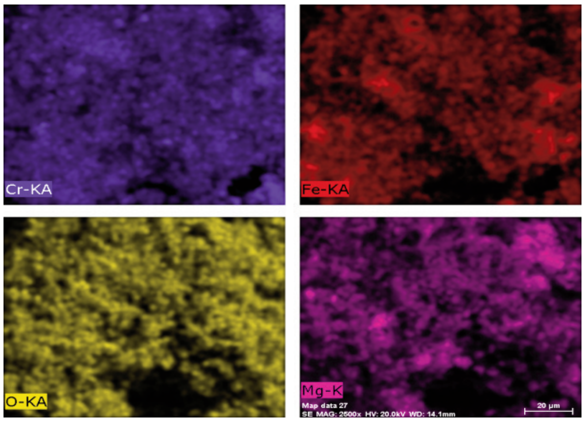


Figure 8. *Reduction degree as a function of time with MgO*



a. with CaO

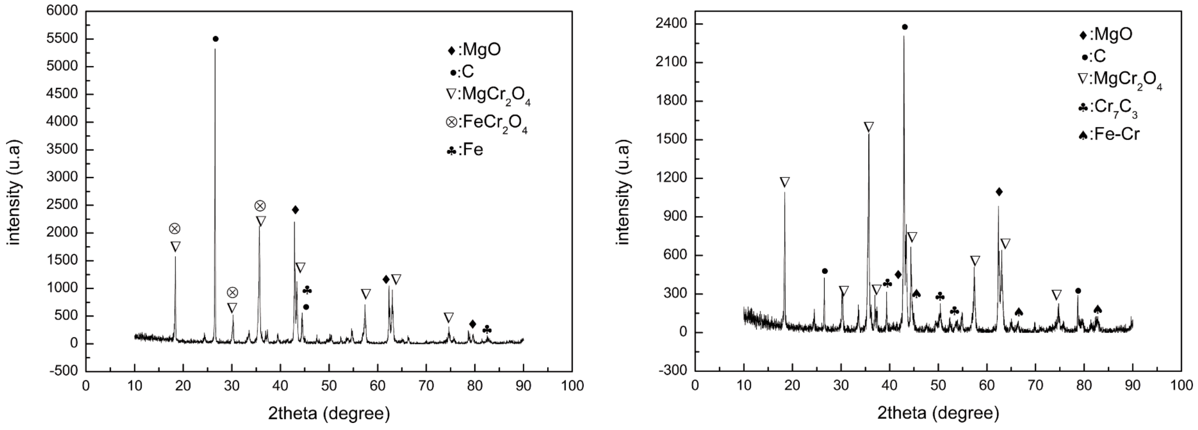


b. with MgO

Figure 10. *Surface scanning for samples with CaO and MgO reduced after 6min*

3.4 Effect of Al_2O_3

Fig. 11 gave the reduction behavior of chromite with Al_2O_3. When the reduction degree was below 30%, addition of Al_2O_3 also revealed a damage effect,



a. 5 min *b. 10 min*

Figure 9. *X-ray patterns of samples reduced after 5min and 10min*

which might also be caused by a dilution influence. Nevertheless, when reduction degree exceeded 30%, Al_2O_3 enhanced the reduction behavior notably. Fig.12 (a) and (b) give the X-ray patterns for reduction proceeding at 2min and 6min respectively. Besides the additive and Fe-Cr, the solid solution of Al_2O_3 with Cr_2O_3 appeared. According to Weber [13], the Al^{3+} could diffuse to the inner core and replace the Cr^{3+}, so the Cr^{3+} could reach the outer zone where it was reduced much easier. So it could be presumed that Al^{3+} would exchange Cr^{3+} and thus enhance both the reduction degree and reduction rate.

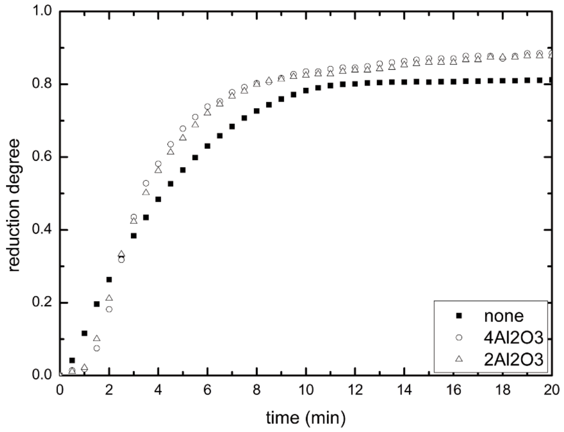


Figure 11. *Reduction degree as a function of time with Al_2O_3*

3.5 Cr metallic kinetics

In our previous study, it has found that the difficulty in reduction of chromate lies in the chromium metallic process. The reduction degree in the chromium oxide reduction step, when the reduction degree went beyond 25%, was found to obey the Zhuravlev-Lesokhin-Tempel's equation, shown in Equation (6), which suggested the reaction was controlled by the ions diffusion in solid phase. The rate constant was determined as 0.03196 from the linear slope.

$$Y = \{1/(1-R)^{1/3} - 1\}^2 = k \cdot t \qquad (6)$$

In the case of various addition presented, the kinetic mechanism was examined again, especially in the chromium metallic process, to figure out the functions of agent in the reduction process. Table 1 gave some kinetic equations used by previous authors that might apply to the reduction of Cr and Table 2 gave the fitting results in present work. Fitting results shown that with CaO and MgO, the Cr metallization was limited by solid diffusion. With Al_2O_3 present, the limiting-step turned to gas-solid diffusion while with SiO_2 nucleation limited the whole process. Figure 13 shows results of linear fitting for the second stage with various additions.

When chromite was reduced with MgO and CaO, the Cr metallization was still limited by the ions diffusion in solid phase. However, CaO could speed up the reduction while MgO would decrease the

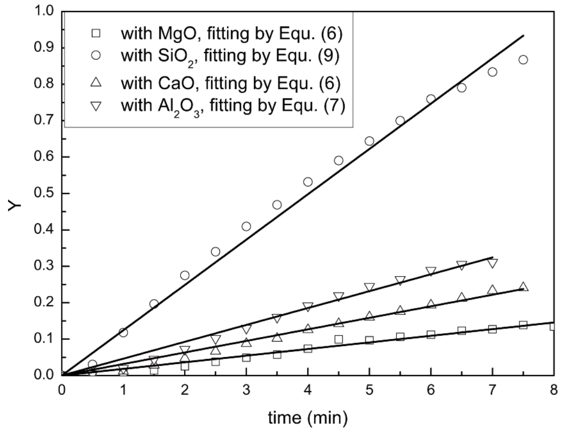
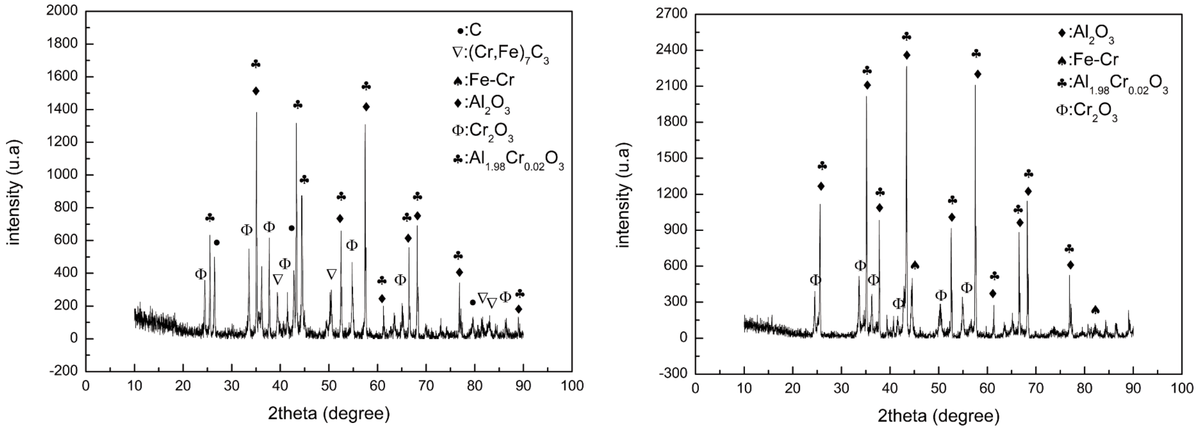


Figure 13. *Linear fitting by respective mechanism for later stage*



a. 2 min *b. 6 min*

Figure 12. *X-ray patterns of samples reduced after 2min and 6min*

Table 1. *Kinetic equations employed in Linear Fitting*

Various reduction kinetics	Equation*		Reference
Solid Diffusion: Zhuravlev-Lesokhin-Tempel's (ZLT)	$Y=\{1/(1-R)^{1/3}-1\}^2=k\cdot t$	(6)	[15, 18]
Gas-solid Diffusion: Ginstling-Brounshtein (GB)	$Y=3-2R-3\times(1-R)^{\frac{2}{3}}=kt$	(7)	[8, 17]
Chemical: contracting spherical reaction	$Y=1-(1-R)^{\frac{1}{3}}=kt$	(8)	[18]
Nucleation: first order reaction	$Y=-\ln(1-R)=kt$	(9)	[15, 18]

**R is reduction degree, k is rate constant, t is time*

Table 2. *Linear fitting results (R square) with different additions in present study*

Addition kind / Equation No.	CaO	MgO	Al_2O_3	SiO_2
6	**0.99425**	**0.99203**	0.96197	0.95109
7	0.9929	0.98822	**0.99394**	0.98198
8	0.96781	0.95278	0.98339	0.99366
9	0.96939	0.9658	0.99189	**0.99689**

reduction rate. As mentioned above, $CaCr_2O_4$ and $MgCr_2O_4$ would both form according to the XRD results, but $MgCr_2O_4$ was much more stable than $CaCr_2O_4$. Meanwhile, since Ca^{2+} could replace the position of Fe^{2+}in spinel, Cr^{3+} cation could diffuse to the periphery area more easily, thus could get contact with the reductive more conveniently. Ding [18] also mentioned that the ZLT equation could describe the latter stage of reduction and CaO could facilitate the solid diffusion process but did not give the mechanism. Meanwhile, when the solid diffusion was strengthened, the gas-solid diffusion mechanism got predominant as well. When the chromite was reduced with MgO, there was a more solid phase $MgCr_2O_4$ formed. It was a pretty stable spinel structure which was more difficult to reduce than $FeCr_2O_4$. Therefore, the Cr^{3+} could be stabilized, which resulted the reduction inhibited. Van Deventer [22] reported that MgO played an inhibiting role in the decomposition of chromite spinel, which was consistent with the present work.

Al_2O_3 also could facilitate the Cr metallization but the rate-limiting step turned to gas-solid diffusion. As mentioned above, the Al^{3+} could replace the Cr^{3+} and form a solid solution with O^{2-}. Under this condition, the Cr^{3+} diffusion could get more easily and the reduction was not limited by it any more. Meanwhile, due to the dilution effect of addition to the chromite, the reducing role of carbon might get weaker. With this indirect reduction happening, the rate-limiting step turned to gas-solid diffusion combined with nucleation. When CO_2 formed, it would contact with solid carbon and form CO again.

Neuschutz [19] reported that complex additions could accelerate the diffusion of Cr by forming liquid slag. In present case of SiO_2, when the reduction degree reached around 50%, that is to say, the trivalent Cr was reduced to divalent, the liquid phase could form, thus the reductive could be transported more easily, so the reaction rate was not limited in the solid diffusion. As confirmed in many previous studies, Cr_7C_3 would form as the reduction product of Cr. In this case, nucleation and/or chemical reaction process would become rate-limiting.

4. Conclusions

The isothermal reductions of $FeCr_2O_4$ with each addition CaO, MgO, Al_2O_3 and SiO_2 were performed at 1673K. Compared with the reduction curve without additions, the reduction rate and the reduction degree were favored with the presence of CaO and Al_2O_3 due to convince the Cr^{3+} diffusion in solid phase. However, the existence of MgO has hampered the reduction since the more stable phase of $MgCr_2O_4$ was formed. Special case occurred in the case of SiO_2, and the reduction degree can still reach the same content as that without addition. However the reduction rate apparently lowered in the Cr metallic process because the liquid phase of CrO-SiO_2 formed, which suggest the smelting reduction happened. The kinetic mechanisms in various cases of additions were also analyzed especially in Cr metallic process. With the presentences of CaO and MgO, the reduction rates in latter stage were still limited in solid diffusion step. However, Al_2O_3 addition could facilitate the Cr metallization but the rate-limiting step turned to gas-solid diffusion. Since a liquid phase of CrO-SiO_2 enhanced the diffusion of chromium ions, the rate determing step came to nucleation and/or chemical reaction process.

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References

[1] D. Fray, J. Min. Metall. Sect. B-Metall. 49 (1) B (2013) 125-130.

[2] N. Barcza: Electric Furnace Proceedings, 1971, 29, 88-93.

[3] Y. Xiao, C. Schuffeneger, M. Reuter, L. Holappa and T. Seppala: ‘Solid state reduction of chromite with CO’, Proc. Int. Ferroalloy Cong., Cape Town, Africa, February 2004, SAIMM, 1-4.

[4] M. Kekkonen, Y. Xiao and L. Holappa: ‘Kinetic study on solid state reduction of chromite pellets’, Proc. Int. Ferroalloy Cong., Trondhein, Norway, June 1995, SAIMM, 351-360.

[5] W. J. Rankin: Arch. Eisenhuttenwes, 1979, 50, 373-378.

[6] H. G. Katayama and M. Tokuda: Trans. Iron Steel Inst. Jpn., 1980, 20, 154-162.

[7] R. Hiltunen and J. Harkki: ‘Reduction Behavior of the Akanvaara Chromite of Northern Finland’, Proc. Int. Ferroalloy Cong., Cape Town, South Africa, February 2004, SAIMM, 36-46.

[8] D. Chakraborty, S. Ranganathan and S. N. Sinha: Metall. Mater. Trans. B, 2005, 36, 437-444.

[9] K. P. D Perry, C. W. P. Finn and R. P. King: Metall. Trans. B, 1988, 19, 677-684.

[10] O. Soykan. R. H. Eric and R. P. King: Metall. Trans. B, 1991, 22, 53-63.

[11] Lekatou and R. D. Walker: Ironmaking & Steelmaking, 1997, 24, 133-143.

[12] P. Weber and R. H. Eric: Metall. Trans. B, 1993, 24, 987-995.

[13] P. Weber and R. H. Eric: Minerals Eng., 2006, 19, 318-324.

[14] P. Weber and R. H. Eric: ‘Solid-state Fluxed Reduction of LG-6 Chromite from the Bushveld Complex’, Proc. Int. Ferroalloy Cong., Cape Town, South Africa, March 1992, SAIMM,71-77.

[15] H. V. Duong and R. F. Johnston: Ironmaking & Steelmaking, 2000, 27, 202-206.

[16] A. Lekatou and R. D. Walker: Ironmaking & Steelmaking, 1997, 24, 133-143.

[17] Y. L. Ding and N. A. Warner: Ironmaking & Steelmaking, 1997, 24: 224-229.

[18] Y. L. Ding and N. A. Warner: Thermochimica Acta, 1997, 292, 85-94.

[19] D. Neuschutz, Janβen, G. Friedricht and A. Wiechowskj: ‘Effect of Flux Additions on the Kinetics of Chromite Ore Reduction with Carbon’, Proc. Int. Ferroalloy Cong., Trondheim, Norway, June 1995, SAIMM, 371-380

[20] Katayama H G, Tokuda M and Ohtani M: Tetsu-to-Hagane (J. Iron Steel Inst. Jpn.), 1986, 72: 1513-1520.

[21] J. Li, G. Bai and G. Li: Chinese Journal of Nonferrous Metals, 2011, 5, 1159-1164.

[22] J.S.J Van Deventer: Thermochimica Acta, 1988, 127: 25-35.

[23] N. F. Dawson, R. I. Edwards, Proc. □ Int. Ferroalloy Congress, 31 August-3 September, Rio de Janeiro, Brazil, 1986, p.105-113.

[24] Y.X. Wang, L.J. Wang and K.C. Chou: Journal of Mining and Metallurgy, 2014, 50: 15-21.

[25] K. C. Mills: Slag Atlas. VDEh 2nd Edition, Verlag Stahleisen GmbH, Düsseldorf, 1995, p. 69.