

KINETICS OF CARBOTHERMIC REDUCTION OF SYNTHETIC CHROMITE

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Abstract

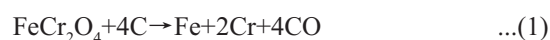
In order to optimize the current reduction process of chromite, a good knowledge of reduction mechanism involved is required. The basic component in chromite ore is $FeCr_2O_4$, thus, kinetic investigation of synthetic $FeCr_2O_4$ with different amount of carbon were carried out in the temperature range of 1473K to 1673K under both isothermal and non-isothermal mode. The iron can be easily reduced compared with chromium. And higher reduction degree of chromite can be achieved by increasing temperature and carbon content. With the supporting of X-ray Diffraction and Scanning Electron Microscope methods, the formation of metallic products followed the sequence: Fe-C alloy, (Fe,Cr)₃C₂ and Fe-Cr-C alloy. Kinetics analysis showed that the first stage was controlled by nucleation with an apparent activation energy of 120kJ/mol, while the chromium reduction was controlled by crystallochemical transformation with an apparent activation energy of 288kJ/mol.

Keywords: Chromite, Carbothermic reduction, Kinetics

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, chromite is often taken into pre-reduction before charged into the submerged arc furnace. Since the pre-reduction process is conducted under a much lower temperature than the submerged arc furnace process, a good knowledge of the solid state reduction behavior of chromite is of great significance. Moreover, the production of ultra-low carbon stainless steel (C<0.03%) is increasingly predominant, which results in the requirement for a better control of the carbon content in the ferroalloy. Up to now, a great amount of work has been carried out to elucidate the reduction behavior of chromite ores from different sources.

According to Perry [1] and Soykan [2], the composition of chromite can be described as a spinel with a formula like $(Fe,Mg)[Cr,Al,Fe]_2O_4$ and the reducible oxides mainly include FeO, Fe_2O_3 , Cr_2O_3 , SiO_2 while the unreducible oxides inside are mainly Al_2O_3 and MgO. Thus, the main reduction can be described by



However, due to the Boudourd reaction, the CO

gas can also act as a reductant and thus the gas product may be CO or CO_2 . In order to figure out the different effect of C and CO, Barcza [3] and Xiao [4] used CO gas to reduce solid chromites and both found that pure CO could not act as a good reductant. However, when solid carbon and CO gas were both employed, high reduction percentage was achieved, which was also confirmed by Kekkonen [5]. Xiao [4] considered that solid carbon helped the transition of CO_2 to CO, while Barcza [3] explain this phenomenon from the effect of solid carbon on the formation of metal carbide because he observed the appearance of intermediate metal carbide and its reducing effect, meanwhile Rankin [6] and Katayama [7] obtained similar conclusion.

In addition, several investigations were focused on the compositions and properties of chromite and different reduction conditions. Hiltunen [8] reported that chromite with low MgO and high FeO was reduced more easily, which was consistent with the findings of Chakraborty [9].

It is worth mentioning the interest to the additional fluxes from researchers. In that there are different gangues in the chromites and during the reduction the gangues are hard to smelt or reduce so investigators attempted to utilize additional fluxes to promote reduction, mainly including SiO_2 [10-15], CaO [16] and fluoride or chloride of alkali metals [17, 18].

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Weber [10-12] and Duong [13] found that SiO_2 could incorporate some non-refractory oxides like MgO and Al_2O_3 to form slag. In this way Cr could be reduced in the slag and further the reduction process. But Lekatou [14] also mentioned too much additives might hinder the contact of chromite and carbon. Ding [16] also investigated the effect of lime and concluded that lime could facilitate reduction. Neuschütz [19] studied compound additives and reported they affected the reactions by facilitating the nucleation or accelerating the diffusion of Cr.

Due to different compositions and properties of chromites, as well as varieties of reduction conditions, investigators gained different kinetics mechanisms, as showed in table 1. Most of them agreed that iron was reduced much more easily than chromium and approximately metalized completely before the start of reduction of chromium. And the reduction of chromium is thus rate-controlling during the whole process. Thus, they divided the reaction to two or three steps and discussed their reduction mechanisms respectively.

This paper focused on the reduction of synthetic pure FeCr_2O_4 , which is the predominant composition of natural chromite. Therefore, compound effect of gangues can be eliminated and a relatively reliable reduction behavior can be represented.

2. Experimental

2.1 Synthesis of pure chromite

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 1100 °C 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 patterns for the synthetic FeCr_2O_4 were shown in Fig. 1, which confirmed the product was pure enough for the conduction of reduction experiments.

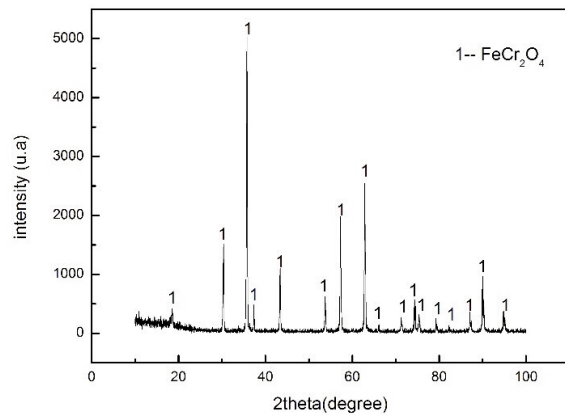


Figure 1. X-ray diffraction patterns for the synthetic FeCr_2O_4

2.2 Reduction of synthetic chromite

Synthetic chromite prepared as above (-200mesh) was mixed with graphite powder (purity 98.5%) and the quantity of carbon was equal to the presumed

Table 1. Different mechanisms gained in literature

Investigator	Additive	Mechanism	Apparent Activation Energy (kJ/mol)
Ding [20]	None	Early stage: nucleation/chemical reaction controlling	114
		Late state: gas/solid diffusion controlling	221
Chak [21]	None	Low temperature: diffusion controlling	
		High temperature: nucleation controlling	
Kekk. [5]	None	unreacted core model with a gas/solid diffusion controlling mechanism	224
Murti. [21]	None	Diffusion of oxygen	57
Lin [22]	None	Early stage: nucleation and growth controlling	270±10
		Middle stage: phase boundary reaction	
		Late stage: diffusion	
Ding [16]	CaO	Early stage: nucleation/chemical reaction controlling	139~161
		Late stage: diffusion of Cr controlling	410
Ding [15]	SiO_2	Early stage: diffusion of ions controlling	194
		Late stage: smelting of Cr controlling	256
Duong [13]	SiO_2	Early stage: nucleation/chemical reaction controlling	172
		Late stage: not sure	

value when the carbon is exactly reacted to form CO as equation (1).

Reduction of synthetic chromite was undertaken by both non-isothermal and isothermal methods. Non-isothermal experiment was conducted using a Netzsch STA449C thermal analysis system with a pretty high accuracy. Thoroughly mixed powder about 100 mg was held in alumina crucible and the experimental temperature was elevated from room temperature to 1773K with a heating rate of 5K/min. Argon gas with a high purity was introduced to the reaction vessel to guarantee a non-oxidizing atmosphere with a flow rate of 80mL/min. And mass of the sample was recorded simultaneously as the reaction proceeded.

Isothermal experiment was conducted using a molybdenum-wire furnace. Reactant powder about 1g was held in alumina crucibles with a volume of 5mL. A thermobalance with an accuracy of 0.001g was used to record the sample weight during the experiment. The molybdenum-wire furnace was heated to the 1473K, 1523K, 1573K, 1623K and 1673K respectively for reduction experiments under argon gas with a flow rate 300 mL/min.

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 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 Non-isothermal experiment

Reduction degree as well as its first order derivative as a function of time were shown in Fig. 2. It was clearly shown that the reduction took place when the temperature was beyond about 1323K, and then the reduction rate increased greatly. However, when the reduction degree reached about 25-30%, the reduction rate gained the first peak. Then the reduction rate began to decrease until at reduction degree of about 60%, it increased again and gained the second peak. After the reduction was nearly completed, the reduction degree could reach about 90%. So it was presumed that during the non-isothermal reduction, there were two stages in which the reduction rate peaked respectively.

3.2 Effect of temperature and time

The reduction fraction of the synthetic chromite at 1473K, 1523K, 1573K, 1623K and 1673K, as calculated from equation (2), was plotted against time in Fig.3. Both reduction rate and reduction fraction

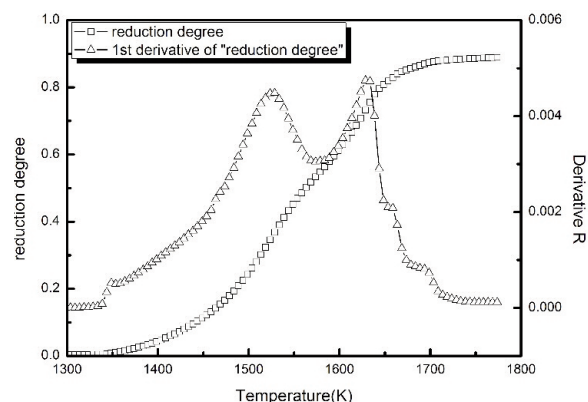


Figure 2. Reduction degree and first deviation as a function of time under non-isothermal condition

increased with increasing time and temperature. When the temperature was increased from 1473K to 1573K, the reduction degree was much improved from nearly 50% to beyond 70%. While increasing the temperature from 1573K to 1673K only improved the reduction degree to nearly 80%. On the other hand, the reduction rate was much improved once the temperature increased by 50K. The reduced samples at different temperature were examined by Scanning Electron Microscope. Images were shown in Fig.4.

In the SEM pictures, it was clearly shown that liquid alloy was formed. The two regions, marked by A and B in both picture turned out to be alloy composed of Fe-Cr-C, but the content of Fe and Cr was different. The darker part contained a higher chromium content. The particles, marked by C, turned to be chromium oxide which remained unreacted. Then, point D and E referred to positions close to the interface between alloy and chromite and EDS showed that it contained a high percentage of chromium and carbon.

As was seen, Fig. 4b presented a much bigger area

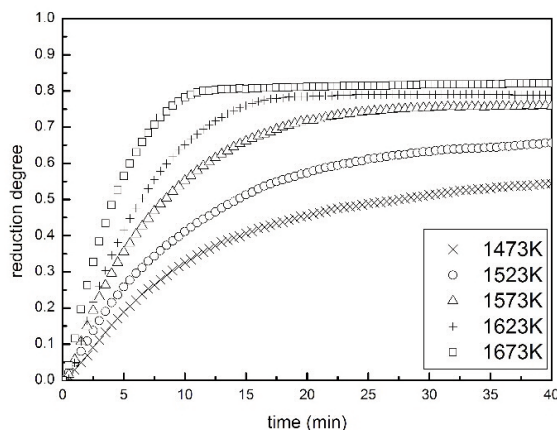


Figure 3. Temperature effect on reduction rate and degree under isothermal condition

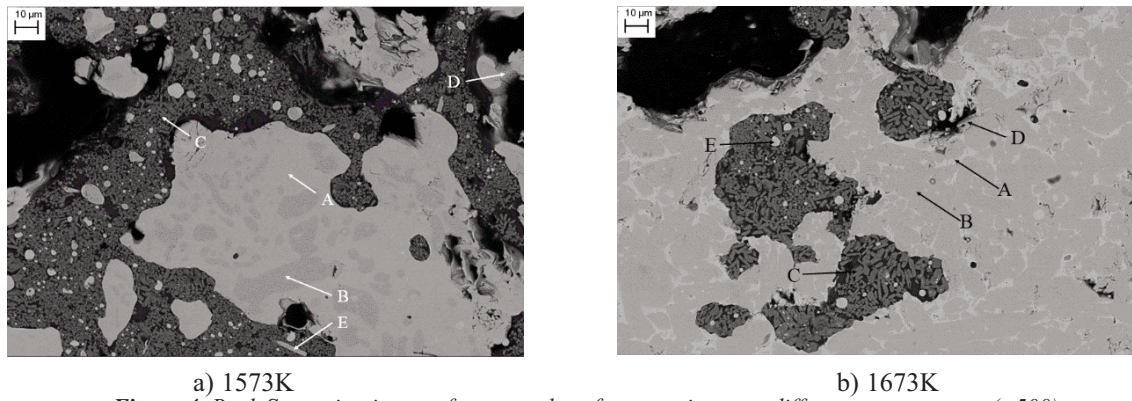


Figure 4. Back Scattering images from samples after experiment at different temperatures ($\times 500$)

of the dark zone, which meant a high chromium metallization. Consistently, the reduction degree curve showed that chromite reduced at 1673K gained a higher reduction degree. Moreover, the unreacted particles did not contain any iron, which confirmed the iron was almost reduced completely before the reduction of chromium taken place. And this result also agreed with the non-isothermal experiment.

Samples reduced at 1573K for 5min($R=31.47\%$) and 15min($R=66.61\%$) were examined by X-ray diffraction as well as Scanning Electron Microscope and the results were shown in Fig. 5 and Fig. 6. It could be seen in the XRD patterns that when the samples were reduced by 5min, there were mostly carbon and slightly Fe-Cr alloy and chromium oxide. With a reduction degree of 31.47%, the sample was found not containing any iron oxide, so the iron had nearly been metallized completely. When the reduction degree reached 66.61%, besides the three contents mentioned above, there was also chromium carbide observed, which was supposed to be the reduction product for chromium.

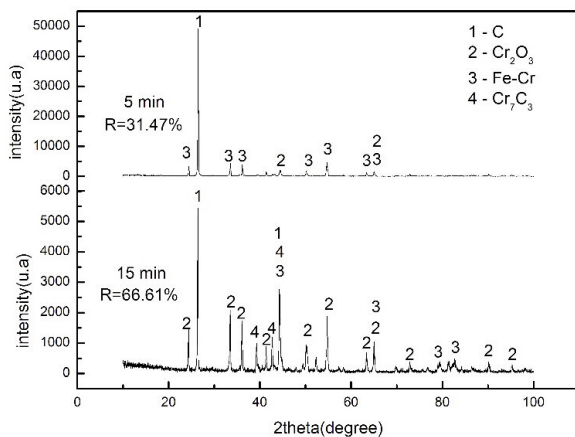


Figure 5. XRD patterns of chromite samples reduced for 5min ($R=31.47\%$) and 15 min ($R=66.61\%$) at 1573K

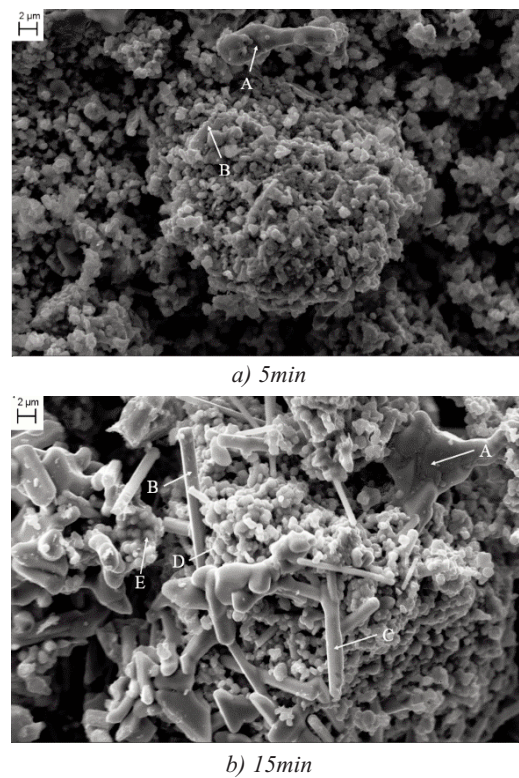


Figure 6. Secondary Electrons images from samples reduced for 5min ($R=31.47\%$) and 15min ($R=66.61\%$) at 1573K ($\times 2,000$)

Table 2. EDS for different points in Fig. 6

point	Contents (atom ratio, %)				
	Fe	Cr	C	O	
5 min					
($R=31.47\%$)	A	29.41	23.33	34.38	12.88
	B	1.19	24.01	16.97	57.83
15 min					
($R=66.61\%$)	A	25.1	74.9	--	--
	B	11.82	32.36	44.12	11.7
	C	12.46	37.07	50.52	--
	D	1.48	18.54	23.26	56.72
	E	1.14	20.31	22.81	55.74

In Fig. 6, micromorphology was found to present obvious difference. Point A in both pictures showed a lump which had a relatively smooth edge and EDS indicated that the oxide content was very low. So with a longer time of reduction, more alloy was formed. But there were also chromium oxide left. The SEM results agreed much well with the XRD observations.

3.3 Effect of carbon content

Fig.7 shows reduction fraction with different carbon content, with the molar ratio 1, 1.1 and 1.2 at 1673K. In the initial stage of reduction, an excess of carbon slightly hindered the reaction rate, which may due to decreasing concentration of $FeCr_2O_4$ caused by a dilution effect of excess carbon. However, when the reduction degree reached about 30%, reduction rate increased greatly with increasing carbon content. Moreover, when the carbon was 20% excess, the reduction degree could reach as high as 95%. So as discussed before, carbon acted in the reaction both as a reactant and as a formation of metal carbide which enhanced the formation of alloy, so when the molar ratio was equal to unit, carbon was not sufficient for a total reduction. An increasing of carbon content in general promoted the reduction degree very largely. The SEM images of reduced samples with carbon content of 10% excess and 20% excess were shown in Fig.8 respectively.

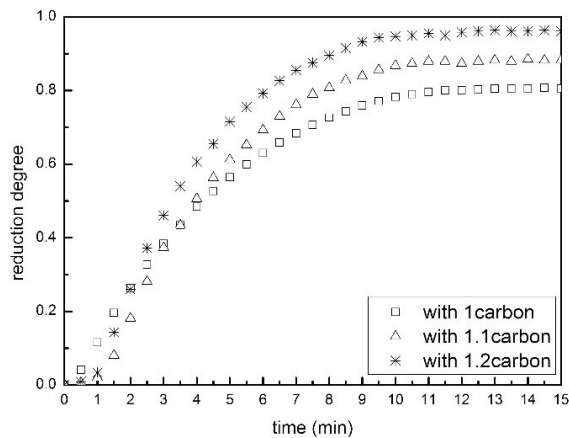
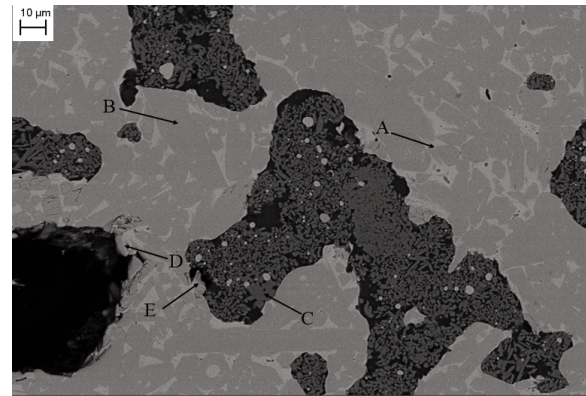
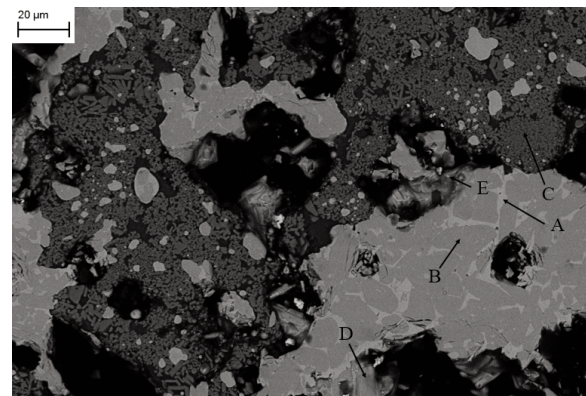


Figure 7. Reduction degree of chromite curves with different carbon content at 1673K

The product was not found much difference from that of the initial sample, mainly including Fe-Cr-C alloy and unreacted chromium oxide. However, it was obvious that higher carbon content resulted in more gas pore, which suggested that increasing carbon content improved the contact between $FeCr_2O_4$ and carbon. Moreover, since carbon acted both reducing agent and carbide former, increasing carbon content could compensate the consumption of carbide, thus enhancing the reduction degree.



a) with 10% excess carbon;



b) with 20% excess carbon

Figure 8. Back Scattering images from samples reduced with different carbon contents at 1673K (× 500)

3.4 Reduction mechanism and kinetics model

According to Lekatou [23], standard free energies of some reactions during reduction of chromite were given in Table 3. It is apparent that the iron oxide can be reduced much easier than the chromium oxide. Moreover, when the quantity of FeO was fixed, the Gibbs free energies of the reaction for different product were basically the same either iron metal or iron carbide was formed. Meanwhile, the iron particles were very easy to be bonded with carbon to form carbide because there was a eutectic point at about 1420K. However, when reduction of chromium oxide began, the product was basically chromium carbide, which is also confirmed by the present study and results of Rankin [6], Katayama [7] and Lekatou [23].

Based on the current study, the reduction mechanism of chromite can be deduced as following steps:

The iron was reduced at very first, with iron or iron carbide formed. Once iron was produced, it would be bound with carbon.

The chromium oxide was reduced by carbon or iron carbide and chromium carbide was formed. And

Table 3. Standard Gibbs free energies of some reactions

No.	Equation	$\Delta G_{1473K}^{\theta}, J$	$\Delta G_{1573K}^{\theta}, J$	$\Delta G_{1673K}^{\theta}, J$
1	$3FeO+4C=Fe_3C+3CO$	-221341.7	-245719.3	-288592.3
2	$3FeO+3C=3Fe+3CO$	-212288.5	-257912.5	-303536.5
3	$21Cr_2O_3+91C=14Cr_3C_2+63CO$	870572.9	-166302.1	-1203198.1
4	$21Cr_2O_3+81C=14Cr_7C_3+63CO$	1016874.9	-19184.1	-1055243.1
5	$21Cr_2O_3+81 Fe_3C=14Cr_7C_3+243Fe+63CO$	1391310.1	437643.1	-516023.9
6	$21Cr_2O_3+63C=42Cr+63CO$	2292171	1271571	250971

with presence of carbon, chromium and iron could melt to form Fe-Cr-C alloy.

When carbon was run out, the reduction was suspended. And there were Fe-Cr alloy and some metallic carbide, and unreduced chromium oxide left.

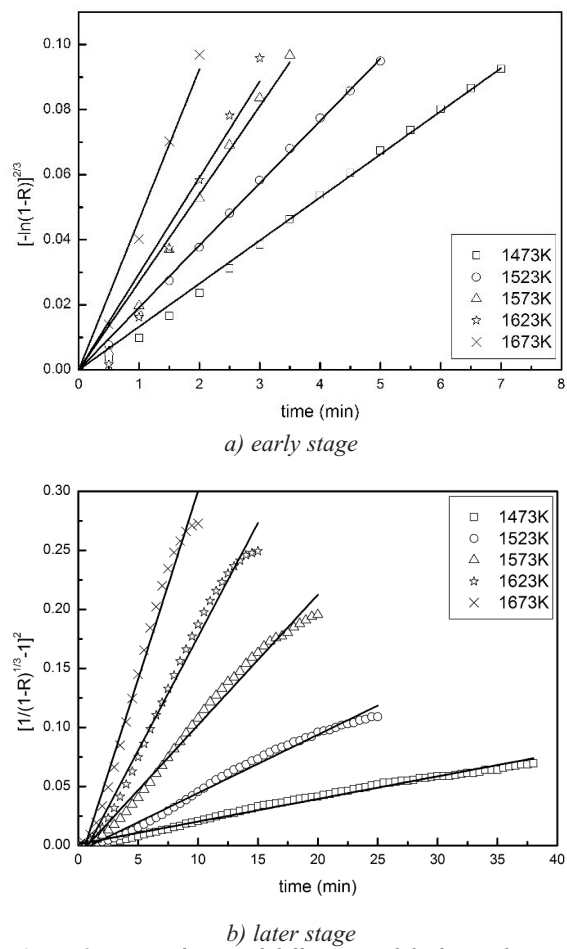
Since the samples used in the experiment were small enough (usually about 1g), the heat transfer was not likely to be the rate-controlling step and was eliminated when the reduction mechanism was analysed. The non-isothermal experiment indicated that the whole reaction taken place probably by two stages. And because the chromite can be represented as $FeO \cdot Cr_2O_3$, the complete reduction of Fe is equal to a reduction degree of 25%. So we divide the reaction to two stages for a better understanding of the reduction mechanism for each step.

The data for the early stage of reduction were found to fit an exponential law for nucleation controlling (equation (3)), while the data for the late stage of reduction were found to fit the equation (4), where R is the reduction fraction, t is the reduction time, and k_1 and k_2 are the rate constants for the early and late stage, respectively. Figure 9 shows results of linear fitting for the two stages.

$$Y1 = [-\ln(1-R)]^2 = k_1 t \quad (3)$$

$$Y2 = \left[\frac{1}{(1-R)^{1/3}} - 1 \right]^2 = k_2 t \quad (4)$$

The calculated apparent activation energy is 120kJ/mol for the early stage and 288kJ/mol for the late stage. And the apparent activation energy of the later stage of the reduction is much larger than that of the early stage. Therefore, the limiting stage is the process of crystallochemical transformation, with predominant influence of temperature on the speed of the process. So it is consistent with the experimental fact that the later stage, which is the metallization of chromium, is the rate limiting step of the whole reduction. Therefore finding ways to enhance the reduction of chromium is of great significance to improve the reduction rate and reduction degree.

**Figure 9.** Linear fitting of different models for early stage and later stage

4. Conclusions

The reduction study of the synthetic chromite at 1473K, 1523K, 1573K, 1623K and 1673K were carried out in the present study. The effect of temperature, carbon content on the reduction degree was discussed, and the mechanism of reduction

process of chromite was also proposed with the supporting of the XRD and SEM analysis results. It is indicated that the reduction process is including two stages: one for iron reduction, the other is for chromium reduction. The reduction degree increases with temperature, time, and carbon content. The iron is reduced much easier than chromium. And the reduction of chromium begins when iron is reduced almost completely. The formation of metallic products follows the sequence: Fe-C alloy, $(\text{Fe,Cr})_7\text{C}_3$ and Fe-Cr-C alloy. The main non-metallic product is unreduced chromium oxide. According to the kinetic analysis, the first stage is controlled by nucleation, in which the apparent activation energy is 120kJ/mol. And the later stage is controlled by crystallochemical transformation with the apparent activation energy of 288kJ/mol. For the aim of improving the reduction degree and reduction rate, the appropriate conditions for the second stage should be optimized accordingly.

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