Chromites Reduction Reaction Mechanisms in Carbon–Chromites Composite Agglomerates at 1 773 K

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Fe–Cr–C production is a very high electrical energy consuming process. When self-reducing agglomerates are used, it is expected to decrease up to 10 % of this electrical energy. This paper presents the fundamental aspects of the reactions involved in reduction of chromites by use of self-reducing agglomerates. Brazilian chromite containing 41.2 % Cr_2O_3 was mixed with petroleum coke and agglomerated with cement as the binder. The concept of “initial slag” was introduced and it was assumed that this “initial slag” is formed of fluxing agents, coke ash, silica formed, binder and dissolution of only 5 % of the gangue from the chromite. This concept is important since the gangue of chromite is composed mainly by refractory oxides ($\text{MgO} + \text{Al}_2\text{O}_3$), which are difficult to dissolve into slag. The effects of “initial slag” composition, one with low liquidus temperature ($\sim 1\,700\text{ K}$) and the other with high liquidus temperature ($\sim 1\,750\text{ K}$) were investigated. The mixture was pelletized, dried and submitted at the temperature of 1 773 K until completion of the reactions and also the fractional reaction as a function of time was determined. The results showed that the pellets in which liquid slag phase was formed at high temperature presented significant better reduction behavior than the pellets in which the liquid slag phase was formed at low temperature. The microscopic analysis showed that a liquid phase was formed but the pellet did not collapse, and indicated that the coalescence of the metallic phase depended on the dissolution of the pre-reduced particles of the chromite into slag.

KEY WORDS: chromite; self-reducing agglomerate; ferro-chromium.

1. Introduction

The current process of ferro-chromium production is performed in the Smelting Arc Furnace (SAF); in order to save energy, composite pellets containing (chromite and coke fines) are currently pre-reduced in a rotary kiln before charging in the SAF. The degree of pre-reduction attained is about 55 % for chromium and 80 % for iron. The remaining reduction reactions and separation of the alloy from the slag usually takes place in the Smelting Arc Furnace.

Fe–Cr–C production is a very high electrical energy consuming process. The theoretical energy requirement for the production of one ton of 55 % chromium alloy at 1 500 K in the solid state is calculated to be about 2 600 kWh, of which about 880 kWh represents the energy necessary to heat the reactants to the process temperature.¹⁾

Figure 1 shows the effect in the net energy consumption as a function of the degree of pre-reduction of chromium for different charging temperatures.

The use of fine chromites and concentrates to the production of ferro-chromium requires their agglomeration for charging into Smelting Arc Furnace (SAF). The self-reducing agglomeration is becoming usual for pre-reducing the chromites and then adding these partially reduced pellets to

the charge into SAF. The advantages of adding this partially reduced chromites are: i) lower electrical energy consumption; ii) use of fines of chromites and of reductants; and iii) better operational control of the SAF.

The technical advantages of these composite agglomerates are: i) the closeness of the reagents and no nitrogen in the reducing gas during the indirect reaction; and ii) improvement of direct reaction at high temperature. Consequently high rate of reduction and higher chromium yield

Fig. 1. Dependence of energy requirement for the production of 1 ton of ferro-chromium on as a function of the pre-reduction degree and charging temperature.¹⁾

can be achieved.

This work intends to improve the knowledge of the carbothermic reduction behavior of the chromites self-reducing pellets, mainly for understanding the reaction mechanisms before and after slag formation. The pre-reduction is normally done at temperatures up to 1 623 K. The important related literature for chromites,²⁾ chromites reduction³⁻⁷⁾ and the concepts on direct and indirect reactions⁸⁾ are also given at the references.

2. Fundamental Aspects of the Reduction Behavior of Chromites

The carbothermic reduction of chromites can occur mainly by³⁾: i) solid chromites is reduced by solid or gaseous reductant; ii) direct reaction at the slag/metal interface, where the dissolved chromites in the slag is reduced by carbon dissolved in the metal phase; and iii) direct reaction between dissolved chromites in the slag and the carbon particles floating on it. Within the mechanism i the direct reduction reaction has been revealed important in self-reducing processes.⁸⁾

In the Smelting Arc Furnace (SAF) the mechanisms ii and iii should be predominant ones. In the self-reducing processes, high benefit is expected when large portion of chromite is reduced by solid or gaseous reductants before liquid phase formation. When the agglomerate forms some liquid phase slag inside the agglomerate, before complete reduction, then undesirable mechanisms ii and iii can be present.

The chromite ore is composed mainly of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $(\text{Cr,Al})_2\text{O}_3$, forming a complex spinelium structure plus some free iron.^{2,4)} Hino^{2,4)} evaluated the activity of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ within a complex solid structure of the type $\text{FeO} \cdot \text{Cr}_2\text{O}_3 - \text{MgO} \cdot \text{Cr}_2\text{O}_3 - \text{MgO} \cdot \text{Al}_2\text{O}_3$ also with presence of $(\text{Cr,Al})_2\text{O}_3$ and observed the negative deviation from ideal behavior, at 1 573 K. They described the $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ activity as a function of the composition and stoichiometry of the unit cell of the chromites at given temperature. The calculated chromites activities were, at 1 473 K, around 0.138 and, at 1 773 K, around 0.173.

The influence of the activities of these chromites is quite sensitive on the minimum temperature for carbothermic reduction from chromites at total pressure of $\text{CO} + \text{CO}_2$ of 1 atmosphere. Taking the activity of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ equal to 0.155, an average value in the temperature range and also considering that the activities of the products of Fe and Cr_2O_3 are unitary, one verifies an increase of the minimum temperature of reduction of iron oxide (FeO) in the structure of the chromite to 1 418 K, with relation to 1 273 K when unitary activity of the chromite is considered. The same behavior occurs when the product is iron carbide (Fe_3C), where the minimum reduction temperature goes up from 1 285 to 1 423 K.

With the same above assumption for chromite activity, the estimated minimum reduction temperatures are: 1 423 K when the reduced product is Cr_7C_3 and 1 496 K when metallic Cr with unitary activity is considered.

For the metal/slag equilibrium, at the final stage of reduction, the C and the Si dissolved in the metal reduce FeO, CrO and SiO_2 contained in the slag. The CrO activity is en-

hanced by increasing the slag basicity, at given temperature. Conventional HCFerCr (High Carbon Ferro Chromium) production in SAF is said to be largely dependent on slag/metal direct reduction reaction but the results of the present work show that the direct reduction by C floating on the slag is also important.

3. Experimental

The following fine materials were used: Brazilian chromite; petroleum coke; Portland cement and fluxing agents (hydrated lime and silica). The fluxing agents were mixed with cement, coke ash and silica so that the liquid slag phase is formed at temperatures of around 1 700 K and 1 750 K, within the concept of “initial slag”. This concept is important for chromite reduction, since after its reduction the remaining gangue is constituted by every refractory oxides, mainly $\text{MgO} + \text{Al}_2\text{O}_3$. Therefore the “initial slag” is hypothetically formed by binder and fluxing agents without computing the dissolution of these refractory oxides. Since some chromites can dissolve to form the slag, for estimation of the “initial slag”, it was assumed that 5% of the gangue from chromite will dissolve into it. The assumption of 5% dissolution of the chromite was based on the presence of around 5% of chromite with particle size less than 44 microns. To assure this assumption the research with chromite classified in different particles size, at narrow range, is going on.

The materials were mixed and pelletized. The pellets were dried and then submitted to reduction tests, using the special system heated by induction and with argon flow of 2 L/min. The cold pellet measuring around 15 mm diameter was placed directly into the graphite crucible pre-heated and stabilized at 1 773 K. They were held there until no gas evolution were observed (around 5 min). The cooling down to room temperature was made also with argon flow. The reaction fraction was determined by weight loss assuming the value of 1 when no gas evolution was observed. The evolution of weight loss along time was determined by interrupting the experiments and cooling the sample. It is not the fractional reduction, since in this case; all the weight loss is included. The graphite crucible size was: internal diameter of 35 mm and internal height of 50 mm. The particle size of the raw materials was all under 0.147 mm.

The apparatus used for the experiments were the same as described elsewhere⁹⁾ and shown in Fig. 2. It consists basically of an induction heated graphite crucible, with controlled atmosphere, with measure of gas evolution.

Fig. 2. System used for the experiments.⁹⁾

Table 1. Chemical composition of the materials (wt%).

Components	Chromite	Petroleum coke	Cement	Fe-Si	Silica	Hydrated lime
Cr ₂ O ₃	41.2					
Fe ₂ O ₃	-		2.78			
FeO	16.9					
SiO ₂	5.7		19.1		100	4
Al ₂ O ₃	17.3		4.92			
MgO	15.6		0.55			31.7
CaO	0.38		64.3			57.4
CaO free			1.01			
Vol. Matter	-	10.8				6.9
Fe total	13.1			25		
P	0.007					
C fix		88.8				
Ash		0.4				
S		0.8				
Si				75		
Ca				0.1		
SO ₂			2.63			
K ₂ O			0.73			
Na ₂ O			0.04			
Others			3.99			

Table 2. Particle size of the materials (% passing).

Sieve mesh	Opening (μm)	Chromite	Pet. coke	Cement	Fe-75% Si	Silica	Hydrated lime
100	147	100	100		100	100	100
150	104	99.3		100	80.8		
200	74	79.0			26.0		
270	53	26.6			4.0		
400	38	2.82			1.37		

Tables 1, 2 and 3 show the physical and chemical characterizations, and composition of the pellet.

Figure 3 and **Table 4** show the scanning electron microscopy image of the chromite and the microanalysis (XEDS) of the components. The particles A and B are chromites, where the chromium content in B is higher than in A. Particle C is a magnesium silicate gangue.

4. Results and Discussion

The estimation of liquidus temperature of the initial slag was based on the assumption that all the binder, fluxing agents, ash from reductant and silicon will form the initial slag with only 5% dissolution of the gangue from chromite. Within these assumptions the “initial slag” composition was calculated and the respective liquidus temperatures of

Table 3. Pellet composition: LLTIS (Low Liquidus Temperature of the “Initial Slag” ~1 700 K) and HLTIS (High Liquidus Temperature of the “Initial Slag”=1 750 K).

Pellet	LLTI	HLTI
	S	S
Liquidus Temperature (K)	1700	1750
	(wt%)	(wt%)
Chromite	57.7	68.2
Petroleum coke (20% excess)	12.0	14.1
Fe-Si (75% Si)	0.83	0.98
Cement	4.50	5.33
SiO ₂	16.2	6.96
Hydrated Lime	8.83	4.35

Fig. 3. Scanning Electron Microscopy of the chromite showing three different components.**Table 4.** Microanalysis (XEDS) of the particles shown in the Fig. 3 (wt%).

	O	Mg	Al	Si	Ti	Cr	Fe
A	28.9	0.83	3.6	-	0.61	27.1	38.9
B	34.4	8.15	9.6	0.01	0.22	35.3	12.3
C	46.2	20.3	0.7	29.2	0.23	0.7	2.67

around 1 700 K and 1 750 K was estimated from quaternary diagram (CaO, MgO, SiO₂ and Al₂O₃).¹⁰⁾

The behavior of the reaction fraction evolution with time of the pellets, for the same experimental conditions (heating rate and final temperature of 1 773 K) is shown in **Fig. 4**. For both pellets, a liquid slag phase was formed, as expected (**Figs. 5, 6 and 7**).

A sensitive difference on fractional reaction with time can be seen in **Fig. 4** when comparing agglomerates with “initial slag” with different liquidus temperatures. Higher reaction fraction is observed for the pellet HLTIS (High Liquidus Temperature of Initial Slag) than that of the pellet LLTIS (Low Liquidus Temperature Initial Slag). The results are credited to: i) for the HLTIS, before “initial slag” starts to form, a large amount of reduction reactions proceeded

Fig. 4. Reaction fraction behavior of pellets with HLTIS and LLTIS, at temperature of 1 773 K.

Fig. 5. Micrograph of the LLTIS pellet, partially reduced (reaction fraction of 0.5), submitted at 1 773 K during 10 min. Continuous slag phase (spot 2); chromite entrapped in the slag phase (spot 3); metallic phase (Fe-Cr-C) (spots 4 and 5); and carbon particle (spot 1) surrounded by Fe-Cr-C (spot 4).

Fig. 6. Same pellet of Fig. 5 (LLTIS) kept during 20 min at 1 773 K. Fractional reaction of 0.53. Almost the same phases and compositions of the phases shown in Fig. 5.

with reactions of solid chromites with C and CO. After slag formation direct reaction is the main mechanism for chromite reduction since chromite particles are entrapped by slag. Dissolved iron oxide and chromium oxide in the slag react with entrapped carbon particles within slag and then follow with reduction of oxides dissolved in slag from carbon containing in Fe-Cr, ii) for LLTIS, the slag is formed much easily and it avoids the continuation of fast

Fig. 7. Micrograph of the HLTIS pellet, with high liquidus temperature of the "initial slag", partially reduced (0.84 of fractional reaction), at 1 773 K, during 10 min.

Table 5. Chemical composition, by XEDS, of the phases shown in Fig. 5, in wt%. LLTIS pellet, during 10 min at 1 773 K.

Phase	O	Mg	Al	Si	Ca	Cr	Fe	C	P	S
1								100		
2	18	12	10	38	17	5.5	0.7	-		
3	11	14	14	.3	.3	43	18	-		
4	-	-	-	.7	-	58	35	4.4	1.3	0.6
5	-	-	-	1	-	10	84	3.2	1.4	0.6

reduction reaction.

The fractional reaction result along time, in Fig. 4, shows that there are at least two important acting mechanisms: very fast reaction in the beginning; and abrupt decrease of reaction rate after the initial liquid slag phase is formed.

The micrographic (Fig. 5) shows the presence of a continuous slag phase and entrapped chromite phase with some white spots of Fe-Cr-C phase, for LLTIS pellets after submitted for 10 min, at 1 773 K. The reaction fraction is low, only 0.5, and the progress of the reaction was very slow. It can be seen that the only few metallic phase was formed within original chromite particles by fast gas/solid reaction. Almost no carbon particles entrapped in the slag was detected. Some reduction happened before liquid slag was formed. With the formation of liquid slag the carbon particles floated to the top of the slag (black particle in Fig. 5). The carbon particles in contact with slag containing dissolved chromite start to nucleate Fe-Cr-C phase around the carbon particles. Direct contact between carbon particles and slag is then avoided but the carbon in the Fe-Cr proceeds with reduction reaction from the slag (Fig. 5). Direct reduction reaction from slag is slower than that by 'direct' and 'indirect' reactions of chromite (initial stage), in self-reducing agglomerates, at the tested conditions (Figs. 4 and 5). The controlling step of this direct reaction from slag is an open question and the research is proceeding. Metallic phase formed before slag formation contains high Fe content (~80%) as shown in Fig. 5 (spot 5, Table 5), and Fig. 6 (spot 3, Table 6) and after slag formation metallic phase contains high Cr content (57%) as it is shown in Fig. 5

Table 6. Chemical composition, by XEDS, of the phases shown in the Fig. 6, in wt%. LLTIS pellet, during 20 min at 1 773 K.

Phase	O	Mg	Al	Si	Ca	Cr	Fe	C
1	20	8.4	12	36	17.7	5.6	0.4	-
2	12	13.6	14.5	0.5	0.3	45.3	14.3	-
3	-	-	-	0.3	-	15.3	80.3	2.2

(phase 4, Table 5) produced by direct reduction. The chromium content in the slag, mainly as CrO, is around 5.5% as shown in Table 5 (phase 2).

From Figs. 5 and 6, and compositions of the phases in Tables 5 and 6, for the composite pellet LLTIS, it can be induced to the following phenomenology: i) in the beginning, when the pellet is heated up to 1 773 K, there is a reduction reaction of chromites mainly of FeO by fast reaction; ii) some Cr is also reduced from chromites together with Fe by indirect reaction and/or by dissolved C in metallic phase (direct reaction); iii) with initial slag formation (liquid phase) the C particles contained in the pellet is segregated, by flotation, to the top of the slag, but some carbon particles can remain entrapped in it; iv) after initial slag formation only direct reaction acts; v) the C particles floating on the slag starts to reduce FeO and CrO dissolved in the slag to Fe and Cr, forming the metallic phase between slag and C particles; vi) the metallic phase surrounding the C particle is increased with C content and reduction reaction continues with metal/slag reaction; vii) chromite particles continue to dissolve into the slag; and viii) dissolved chromite in the slag diffuses to the slag-metal interface.

Figure 7 shows morphologies of the phases, of the HLTIS self-reducing chromites pellets, submitted at 1 773 K during 10 min, with reaction fraction of 0.84. It can be seen that initial liquid slag phase was also formed, as expected (spot 3 in Fig. 7), but was not enough to float the C particles. Most of the C particles remained entrapped in the slag which proceeded with direct reduction reaction (metal/slag) forming the large metallic phase (spot 1, white phase surrounding carbon particle in Fig. 7). One can observe that with this high liquidus temperature of the “initial slag” the contribution of the fast reduction reaction during the initial step, before slag formation, is much more intense achieving high degree of reduction (small white particles inside of the original chromites particles, in Fig. 7) in comparison with that of the LLTIS pellet (Fig. 5). Therefore the chromite reduction is enhanced by avoiding the premature slag formation.

For the HLTIS (Fig. 7) the chromium content in the metallic phase reached ~60 wt% (Table 7) confirming the fractional reaction of 0.84. The contents of chromium and iron in the slag were, for both, around 0.8%, which are very low. The metallic phase in Fig. 7 (HLTIS), 10 min at 1 773 K, shows more coalescence than that in Fig. 5 (LLTIS), 10 min at 1 773 K.

5. Conclusions

The following conclusions are derived for carbothermic

Table 7. Chemical composition, by XEDS, of the phases shown in the Fig. 7, in wt%. HLTIS pellet, during 10 min, at 1 773 K.

Phase	O	C	Mg	Al	Si	P	S	Ca	Cr	Fe
1	-	3.7	0.7	0.9	1.1	1.3	0.4	0.3	61	34
2	20	-	38	1.5	33	2.2	0.2	1.5	0.5	0.8
3	17	-	6.9	13	31	1.3	1.0	28	0.9	0.4
4	18	-	4.7	12	32	1.5	1.9	30.	0.5	0.6

reduction reactions of self-reducing agglomerates of chromites, at temperatures in which slag is formed but it is not enough to segregate in layers of slag and non dissolved solids. After experiments, the agglomerated remained almost with the same original form, containing the continuous slag phase with solid particles of chromites and carbon entrapped in it.

(1) The carbothermic reduction reaction of chromites in self-reducing agglomerates, at temperatures in which slag is formed, present two mechanisms. One, in the beginning, with fast reaction rate before slag formation in the agglomerate and the other slower reaction rate after slag formation.

(2) Initially the continuous phase of slag is formed only with little dissolution of chromites. Most of chromites and carbon particles (solid) remain entrapped in the slag.

(3) The initial step of fast reaction rate is due mainly to the gas/solid indirect reaction and direct reaction. When slag is formed in the agglomerate then the reaction mechanism is due only to slower slag/metal direct reaction (carbon dissolves in metallic phase and then reduces Fe and Cr from the slag).

(4) When the agglomerates have components which form “initial slag” at low or high temperatures, at the same reduction temperature, then faster reaction occurs with that of high liquidus temperature of “initial slag” than that of agglomerate with low liquidus temperature of “initial slag”.

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