



Original Article

High carbon ferro-chromium by self-reducing process: Fundamentals

Adolfo Pillihuaman Zambrano*, Cyro Takano, Alberto Eloy Anduze Nogueira
and Marcelo Breda Mourao

Department of Metallurgical and Materials Engineering, Escola Politécnica of the University of Sao Paulo,
Av. Prof. Mello Moraes, 2463 – Sao Paulo – SP - 05508-900 Brazil.

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Abstract

Fe-Cr-C production is a very high electrical energy consuming process. When self-reducing agglomerates are used, it is expected to reduce up to 10% of this electrical energy. This paper presents the fundamental aspects of the reactions involved for reduction of chromites from self-reducing agglomerates. Brazilian chromite containing 41.2%Cr₂O₃ 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 by fluxing agents, coke ash, silica, binder and only dissolution of 5% of the gangue from the chromite. This concept is important since the gangue of chromite is composed mainly of refractory oxides (MgO+Al₂O₃), which are difficult to dissolve into slag. The effects of “initial slag” composition, one with low *liquidus* temperature (~1700K) and other with high *liquidus* temperature (~1750K) were investigated. The mixture was pelletized, dried and submitted to a temperature of 1773K until completion of the reaction. The reaction fraction as a function of time was determined. The results show that pellets containing components with liquid slag phase formed at higher temperature presented significant better reduction behavior than pellet with the liquid slag phase formed at lower temperature. The scanning electron microscopy analysis showed that a liquid phase was formed but the pellet did not collapse and indicated that the coalescence of the metallic phase depends on the dissolution of the pre-reduced particles of the chromite into slag.

Keywords: chromite, self-reducing agglomerate, ferro-chromium

1. Introduction

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

- 1) Lower electrical energy consumption;
- 2) Use of fines of chromites and of reductants; and
- 3) Better operational control of the SAF.

The technical advantages of these composite agglomerates are: 1) closeness of the reagents and no nitrogen in the reducing gas during the indirect reaction; and 2) direct reaction improvement at high temperature. Consequently, high rate of reduction and higher chromium yield can be achieved.

This work intends to improve the knowledge of the carbothermic reduction behavior of the Brazilian chromite self-reducing pellets, mainly for the understanding of the reaction mechanisms before and after slag formation. The pre-reduction is normally done at temperatures up to 1623K. The important related literature for chromites (Hino *et al.*, 1995), chromites reduction (Rankin 1979; Hino *et al.*, 1988; Akyuzlu *et al.*, 1994; Katayama 1977; Katayama *et al.*, 1984) and the concepts on direct and indirect reactions (Meng *et al.*, 2003) are emphasized.

*Corresponding author.

Email address: cytakano@usp.br

2. Thermodynamic estimation on the reduction behavior of chromites

The chromites carbothermic reduction can occur mainly (Rankin, 1979):

- 1) when solid chromites are reduced by solid or gaseous reductant;
- 2) in direct reaction on slag/metal interface, where dissolved chromites on slag are reduced by carbon dissolved on metal phase; and
- 3) in direct reaction between dissolved chromites on slag and carbon particles floating on it.

Within the mechanism **1** the direct reduction reaction has been important in self-reducing processes (Meng *et al.*, 2003).

At the Smelting Arc Furnace (SAF) the mechanisms **2** and **3** should be predominant ones. At the self-reducing processes, high benefit is expected when large portion of chromium 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 **2** and **3** can result.

Chromite ore is composed mainly of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, and $(\text{Cr}, \text{Al})_2\text{O}_3$, forming a complex spinelium structure plus some free iron (Hino *et al.*, 1995; Rankin 1979; Hino *et al.*, 1988). Hino *et al.* (1988; 1995) evaluated the activity of the $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ 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 $(\text{Cr}, \text{Al})_2\text{O}_3$ and observed negative deviations from ideal behavior, at 1573K. They described the $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ activity as a function of composition and stoichiometry of the unit cell of the chromites at given temperature. The calculated chromites activities were approx. 0.138 at 1473K, and approx. 0.173 at 1773K.

The influence of these chromites activities is quite sensitive on the minimum temperature for carbothermic reduction from chromites ores at a total pressure of $\text{CO} + \text{CO}_2$ of 1 atmosphere. For the products Fe and Cr_2O_3 obtained by carbothermic reaction from chromite, the minimum reduction temperature is 1273K, when unitary activities are considered. This temperature increases to 1418K when the chromite activity is 0.155 (average value). The same behavior occurs when the products are iron carbide (Fe_3C) and chromium oxide (Cr_2O_3), where the minimum reduction temperature goes from 1285K to 1423K.

With the same above assumption for chromite activity, the estimated minimum reduction temperatures are: 1423K when the reduced product is Cr_7C_3 and 1496K when metallic Cr with unitary activity is considered.

For 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. CrO activity is enhanced by increasing the slag basicity, at a 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 the C floating on the slag is also important.

3. Experiment setup

The following fine materials were used: Brazilian chromite; petroleum coke; Portland cement and fluxing agents (hydrated lime and silica). The fluxing agents were added to combine with cement, coke ash and silica such that liquid slag phase is formed at temperatures around 1700K and 1750K, within the concept of "initial slag". This concept is important for chromite reduction, since after its reduction the remaining gangue consists of 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 chromite 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 materials were mixed and pelletized. The pellets were dried and then submitted to reduction tests, using the special system heated by induction and passing into the furnace an argon flow of 2 l/min. The cold pellets were placed directly into the graphite crucible pre-heated and stabilized at 1773K for a feeding system. They were held there for 5, 10, 20, 40, 120 and 180 minutes duration and the gas evolutions were observed. Rapid cooling down to room temperature was made with argon flow. The reaction fraction was determined by weight loss taking as reference to the experience that resulted in no chromium in slag. Reaction fraction at instant t was calculated applying equations 1 and 2.

$$Fr = M1 / M \quad (1)$$

$$M1 = (Mi - Mt) / Mi \quad (2)$$

where:

- Fr : reaction fraction at instant t;
- Mi : initial weight of dried pellet;
- Mt : weight of pellet at instant t;
- M : maximum reaction fraction.

The graphite crucible has an internal diameter of 35 mm and the internal height of 50 mm. The particle sizes of the fine materials were all under 0.147 mm.

The apparatus used for the experiments was the same as described by (Mourao 2000) and is shown in Figure 1. It consists basically of an induction heated graphite crucible, with controlled atmosphere plus measurement of gas evolution.

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

Figure 2 and Table 4 show, respectively, the scanning electron microscopy image of the chromite and the microanalysis (XEDS) of the components. Particles A and B are

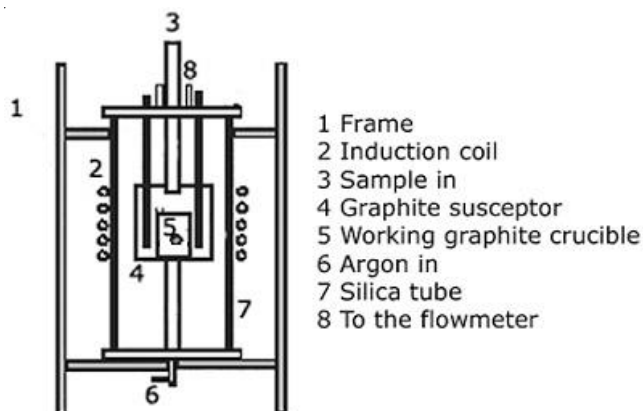


Figure 1. System used for the experiments. (Mourao, 2000).

chromite, where the chromium content in B is higher than in A. Particle C is a magnesium silicate gangue.

4. Results and Discussions

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. The estimation of such slag composition is given in Table 3 for the *liquidus* temperatures of around 1700K and 1750K.

The behavior of the reaction fraction evolution with time of the pellets, for the same experimental conditions (heating rate and final temperature of 1773K) is shown in Figure 3. For both pellets, a liquid slag phase was formed, as expected (Figures 4, 5 and 6).

A sensitive difference on reaction fraction with time can be seen in Figure 3 when comparing agglomerates with *initial slag* and different *liquidus* temperatures. Higher reaction fraction is observed for the pellet HLTIS (High *Liquidus* Temperature of *Initial Slag*) than of that with the pellet LLTIS (Low *Liquidus* Temperature *Initial Slag*). These results are due to these reasons:

Table 1. Chemical composition of 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 materials (% passing)

Sievmesh	Opening(μm)	Chromite	Pet.coke	Cement	Fe-Si	Silica	Hydratedlime
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		

Table 3. Pellet composition: LLTIS (Low Liquidus Temperature of Initial Slag ~1700K) and HLTIS (High Liquidus Temperature of Initial Slag = 1750K)

Pellet	LLTIS	HLTIS
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

1) For the HLTIS, before an *initial slag* starts to form, a large amount of reduction reactions precedes by reactions of solid chromite 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 the slag and then follow by reduction of oxides dissolved in slag from carbon containing in Fe-Cr.

2) For LLTIS, the slag is formed much easily and it avoids the continuation of fast reduction reaction.

The reaction fraction results with time, in Figure 3, show that there are at least 2 important acting mechanisms:

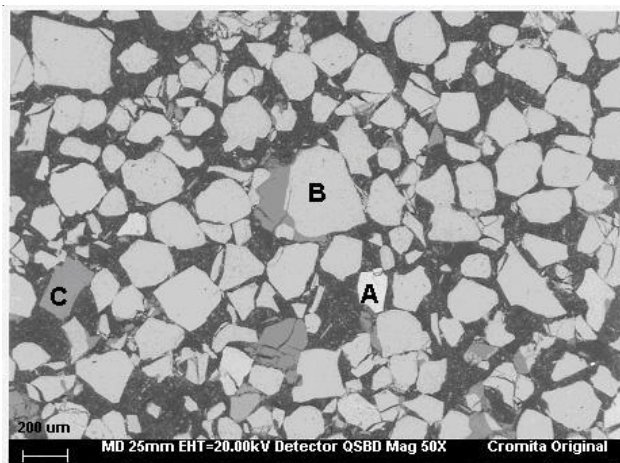


Figure 2. Scanning Electron Microscopy of the chromite showing three different components.

Table 4. Microanalysis (XEDS) of the particles shown at Figure 2 [1]. (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

very fast reaction in the beginning; and abrupt decrease in reaction rate when the *initial liquid slag* phase is formed.

Figure 4 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 minutes, at 1773K. The reaction fraction is low, only 0.5, and the progress of the reaction was very slow. It can be seen

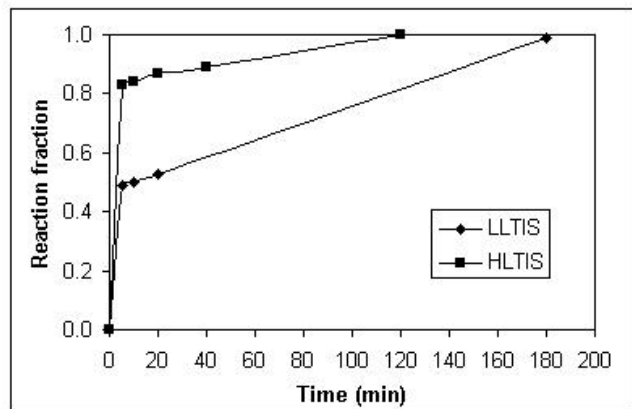


Figure 3. Reaction fraction behavior of pellets with HLTIS and LLTIS, at temperature of 1773K

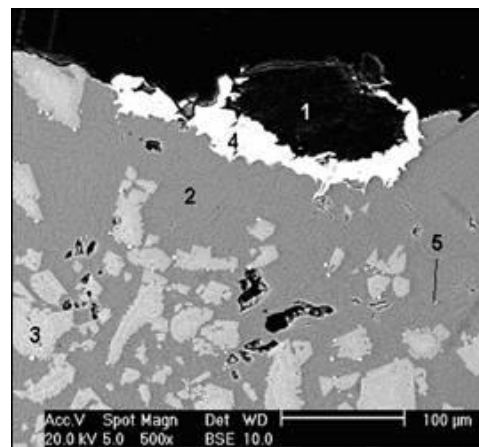


Figure 4. Micrograph of the LLTIS pellet, partially reduced (reaction fraction of 0.5), submitted to 1773K for 10 minutes duration. Continuous slag phase (spot 2); chromite entrapped in the slag phase (spot 3); metallic phase (Fe-Cr-C) (spots 4 and 5); and carbon particle (spot 1) surrounded by Fe-Cr-C (spot 4).

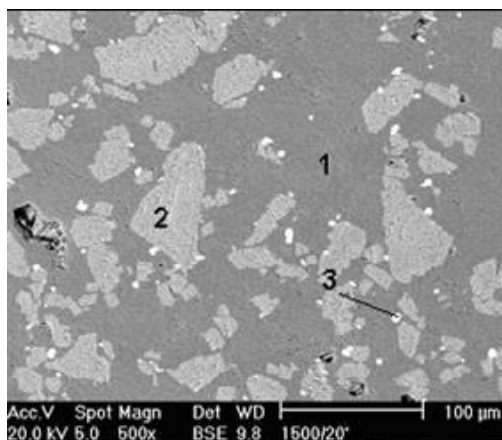


Figure 5. Same pellet of Figure 4 (LLTIS) kept for 20 minutes duration at 1773K. Reaction fraction of 0.53. Continuous slag phase (spot 1); chromite entrapped in the slag phase (spot 2); metallic phase (Fe-Cr-C) (spot 3).

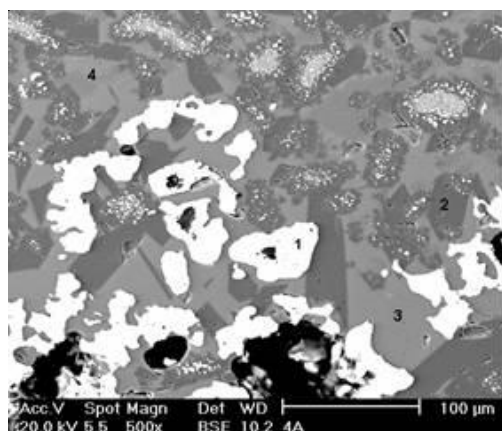


Figure 6. Micrograph of the HLTIS pellet, with high liquidus temperature of the initial slag, partially reduced (0.84 of fractional reaction), at 1773K, for 10 minutes duration. Continuous slag phase (spots 2, 3 and 4); metallic phase (Fe-Cr-C) (spot 1).

that little metallic phase was formed within original chromite particles by fast gas/solid reaction. Carbon particles entrapped in the slag was not detected. Some reduction occurred before liquid slag was formed. With the formation of liquid slag the

carbon particles floated to the top of the slag (black particle in Figure 4). The carbon particles in contact with slag containing dissolved chromite act as nuclei for the Fe-Cr-C phase. Direct contact between carbon particles and slag is then avoided but the carbon in the Fe-Cr proceeds with reduction reaction from the slag (Figure 4). Direct reduction reaction from slag is slower than by 'direct' and 'indirect' reactions of chromite (initial stage), in self-reducing agglomerates, under the test conditions (Figure 3 and Figure 4). 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 Figures 3 and 4 (spot 5, Table 5; and spot 3, Table 6) and after slag formation the metallic phase contains high Cr content (57%) as shown in Figure 4 (phase 4, Table 5) to have been 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 Figures 4 and 5, and compositions of phases in Tables 5 and 6, for the composite pellet LLTIS, it can be deduced that:

- 1) In the beginning, when the pellet is heated up to 1773K, there is a reduction reaction of chromite mainly of the Fe by fast gas/solid reaction;
- 2) Some Cr is also reduced, in this step, from chromite together with Fe by indirect reaction and/or by dissolved C in metallic phase (direct reaction);
- 3) 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;
- 4) After *initial slag* formation only direct reaction occurs;
- 5) The C particles floating on the slag start to reduce Fe and Cr from FeO and CrO dissolved in the slag, forming the metallic phase between slag and C particles; and
- 6) The metallic phase surrounding the C particle increased with C content and the reduction reaction continued with metal/slag reaction.

Figure 6 shows the phases and morphologies of the phases, of the HLTIS self-reducing chromite pellets, submitted at 1773K for 10 minutes duration, with reaction fraction of 0.84. It can be seen that *initial liquid slag* phase was also formed, as expected (spot 3 in Figure 6), but was not enough

Table 5. Chemical composition, by XEDS, of the phases shown at Figure 4, in wt%. LLTIS pellet, for 10 minutes duration at 1773K.

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

Table 6. Chemical composition, by XEDS, of the phases shown at Figure 5, in wt%. LLTIS pellet, for 20 minutes duration at 1773K.

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

Table 7. Chemical composition, by XEDS, of the phases shown at Figure 6, in wt%. HLTIS pellet, for 10 minutes duration, at 1773K.

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

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 Figure 6). 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 (small white particles inside the original chromites particles, in Figure 6) comparing to that of the LLTIS pellet (Figure 4). Therefore the chromite reduction is enhanced by avoiding the premature slag formation.

For the HLTIS (Figure 6) the chromium content in the metallic phase reached ~60wt% (Table 7), confirming the reaction fraction 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 Figure 6 (HLTIS), 10 minutes at 1773K, shows more coalescence than with that of Figure 4 (LLTIS), 10 minutes at 1773K.

5. Conclusions

For the experimental conditions used it can be concluded that:

1. The carbothermic reduction reaction of chromite in self-reducing agglomerates, at temperatures in which slag is formed, presents two mechanisms: the former with fast reaction rate before slag formation in the agglomerate, and the latter slower reaction rate after slag formation.

2. In the *initial slag* there is little dissolution of chromite. Most of the chromite and carbon particles (solid) remain entrapped in the slag in this step.

3. The initial step of fast reaction rate is due mainly to the gas/solid indirect reaction and direct solid/solid reaction. When slag is formed in the agglomerate then the

reaction mechanism is due only to slower slag/metal direct reaction (carbon dissolves in the metallic phase and then reduces Fe and Cr from the slag).

4. When the agglomerates have components which form *initial slag* at lower or higher temperatures, at the same reduction temperature, then faster reaction occurs at that of higher *liquidus* temperature of *initial slag* than with that of agglomerate at lower *liquidus* temperature of *initial slag*.

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