

REDUCTION BEHAVIOR OF CHROMITE CARBON COMPOSITE PELLETS, AT TEMPERATURE OF 1873K ¹

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Abstract

Pre-reduced ferrochromium with high recovery yield of chromium is expected to decrease the overall energy consumption for ferrochromium production. The advantages of pre-reduced in comparison with lump ore in charging electric furnace for ferro-chromium production are: i) low consumption of electric energy; ii) use of fines of chromite and reductant; iii) better operational control of the electric furnace. The self-reducing pellets containing Brazilian chromite (Jacurici concentrate), petroleum coke and 2% Fe-75%Si, were agglomerated with Portland cement. For each experiment ~200g of pellets was used and they were placed at reduction zone (1773K) in a laboratory rotary kiln furnace. Experiments with 5, 10 and 30 minutes were made. The reduced pellets were analyzed by scanning electronic microscopy and it was observed: practically complete reductions of Cr and Fe; formation of a continuous slag phase at 30 minutes; a pre-reduced with compression strength of 130 kgf and without re-oxidation. The results have shown a great potential for use of this self-reducing process for high carbon ferro-chromium production.

Key words: Chromite; Self-reducing agglomerate; Ferrochromium.

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1 INTRODUCTION

The use of fine chromites and concentrates to the production of ferrochromium requires their agglomeration for charging into Smelting Arc Furnace (SAF). Within the agglomeration the self-reducing agglomerates is becoming usual for pre-reduction and then adding to the charge into SAF. The advantages of charging this pre-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⁽¹⁾.

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) improve direct reaction at high temperature. Consequently high rate of reduction and higher chromium yield can be achieved. The pre-reduction is normally done at temperatures up to 1623K.⁽¹⁾

1.1 Use of Pre-Reduced to Produce High Carbon Ferro-Chromium Alloy

The high carbon ferro-chromium is usually produced by the reduction of chromium ore (chromite), with carbon, normally coke, in electric arc furnace. The energy consumption is 3,500 – 4,000 kWh/t of high carbon ferro-chromium and the recovery yield is approximately 90% Cr. The high consumption of electric energy increases the production cost. In industrial processes the self-reduced pellets or briquettes of chromite pre-reduced at level of 55% of Cr and 80% of Fe are charged by gravity into submerged arc furnace to produce the high carbon ferro-chromium alloy.

The theoretical energy saved when a pre-reduced (at reduction degree of 55% for Cr) is charged is shown at Figure 1. The electric energy saving can reach around 2000 kWh/t of ferro-chromium. The preheating of the charge can save around 600 kWh/t.

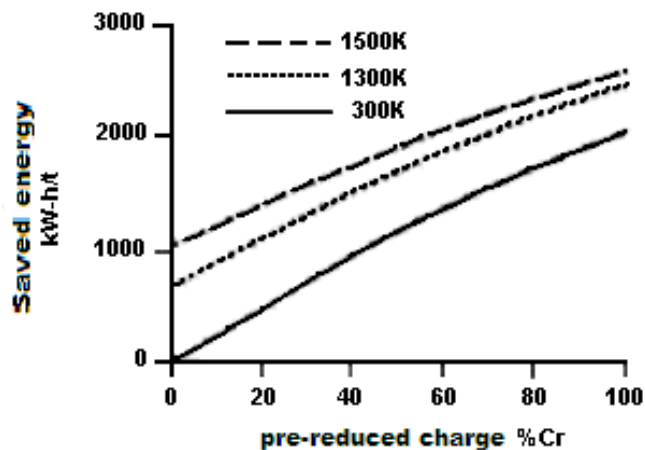


Figure 1. Electric energy savings with pre-reduced and preheated charges for high carbon ferro-chromium production (HCFerCr)⁽¹⁾

1.2 Reduction Behavior of Chromite

The carbothermic reduction of chromites can occur mainly by:⁽²⁾ i) solid chromites is reduced by solid or gaseous reductant; ii) direct reaction by slag/metal, 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 the self-reducing processes.⁽³⁻⁶⁾

In the Smelting Arc Furnace (SAF) the mechanisms ii and iii should be predominant ones. In the self-reduction 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 not desirable mechanisms ii and iii can be present.

Taking the activity of the $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ equal to 0.155,^(7,8) an average value between the temperature range and also considering that the activities of the products Fe and Cr_2O_3 are unitary, verifies an increase of the minimum temperature of reduction of iron oxide (FeO) present in the structure of the chromite to 1418K, with relation to 1273K when unitary activity of the chromite is considered. The same behavior occurs when the product is an iron carbide (Fe_3C), where the minimum reduction temperature goes up from 1285K to 1423K.

This paper tries to observe the behavior of carbothermic reduction the self-reducing pellets of chromite with additions to 2% of Fe-Si,^(5,6) when they are charged to an experimental rotary kiln furnace at 1773K .

2 EXPERIMENTAL

The following fine materials were used: Brazilian chromite (Jacurici concentrate), petroleum coke, ferro-silicon and Portland cement. The materials had been mixed and pelletized. The pellet composition is in the Table 1. Tables 2 and 3 show the particle size distribution and chemical analysis of the materials. The Figures 2 and 3 present a view and scheme of the furnace. After drying (393K for 24 hours) in a stove, the pellets (~200 g) were submitted to experiments, in the laboratory rotary kiln furnace (Figure 2) heated by electric source. It has two concentric tubes. Into of the alumina tube another tube of high density graphite was placed. The thermal profile of 1773K shown in the Figure 3 was used, with argon flow (2L/min). The pellets, at room temperature, were charged from one side and the slope was controlled to keep the residence time of 5, 10 and 30 minutes, at 1773K (high temperature zone). The pellets were pre-heated at the charging side, reduced at the reaction zone and partially cooled at discharging side. The product was collected in a steel box for further microscopic and XEDS analysis.

Table 1. Pellet composition (wt %):

Chromite	76.00
Petroleum coke	17.00
Fe-Si (75%Si)	2.00
Cement	5.00

Table 2. Particles size of the materials (% cumulative)

Sieve (Mesh)	Opening (μm)	Chromite	Petroleum coke	Cement	Fe-75%Si
100	147	100	100		100
150	104	99.25		100	80.77
200	74	79.04			25.96
270	53	26.61			3.96
400	38	2.82			1.37
-400		0.00			0.00

Table 3. Chemical composition of the materials (wt %)

Components	Chromite	Petroleum Coke	Cement	Ferro-silicon
Cr ₂ O ₃	41.2			
Fe ₂ O ₃	-		2.8	
FeO	16.9			
SiO ₂	5.7		19.1	
Al ₂ O ₃	17.3		4.9	
MgO	15.6		0.6	
CaO	0.4		64.3	
CaO free			1.0	
M. Volatile	-	10.8		
Fe total	13.1			25
P	0.007			
C fixed		88.8		
Ash		0.4		
S		0.8		
Si				75
Ca				0.14
SO ₂			2.6	
K ₂ O			0.7	
Na ₂ O			0.04	
Other			4.0	



Figure 2. System used for the experiments (laboratory rotary kiln furnace, electrically heated).

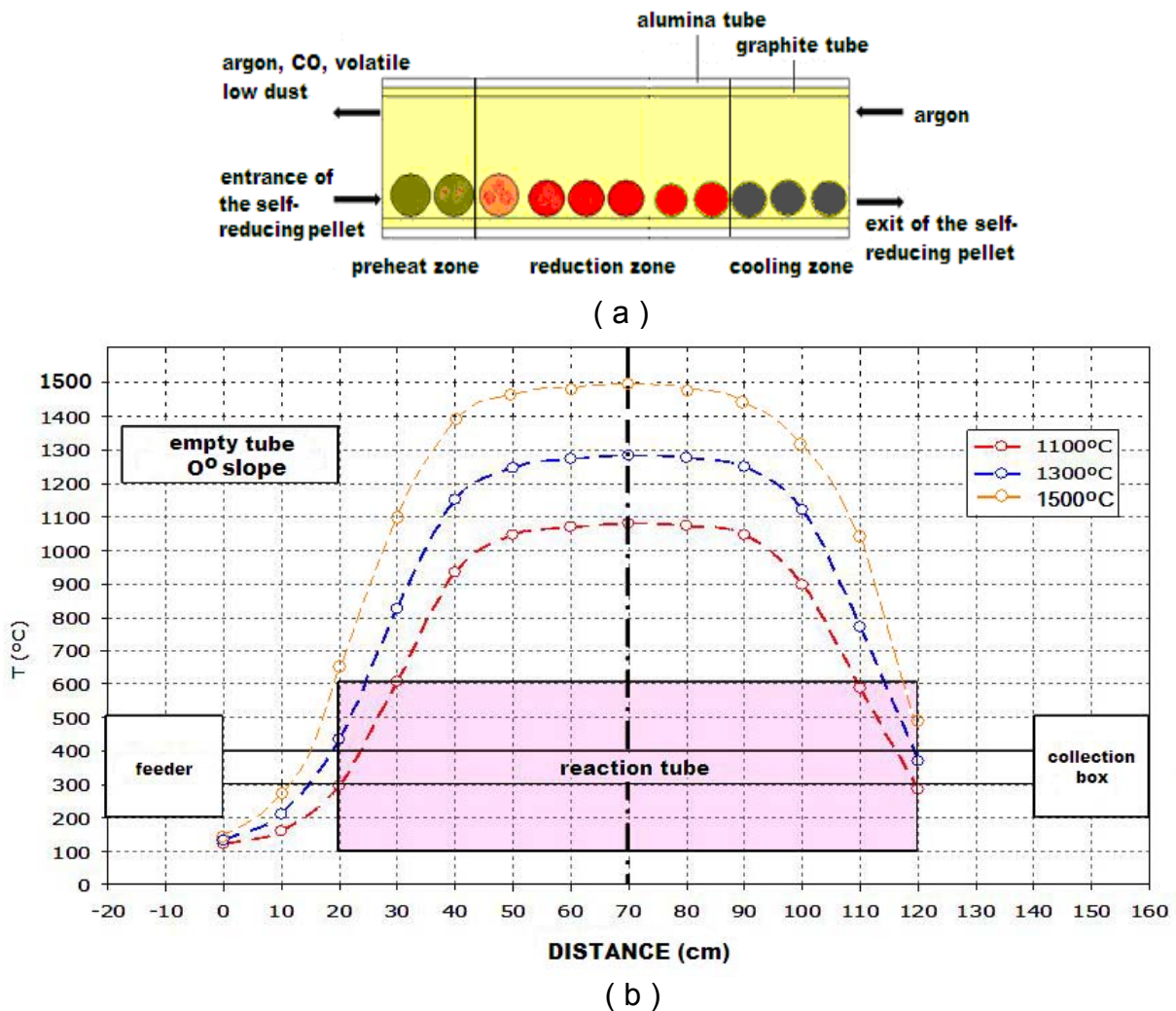


Figure 3. (a) Scheme the reduction process in the laboratory rotary kiln furnace. (b) Thermal profiles the laboratory rotary kiln furnace with 0° slope.

The Figure 4 and Table 4 show the scanning electron microscopy image of the chromites 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.

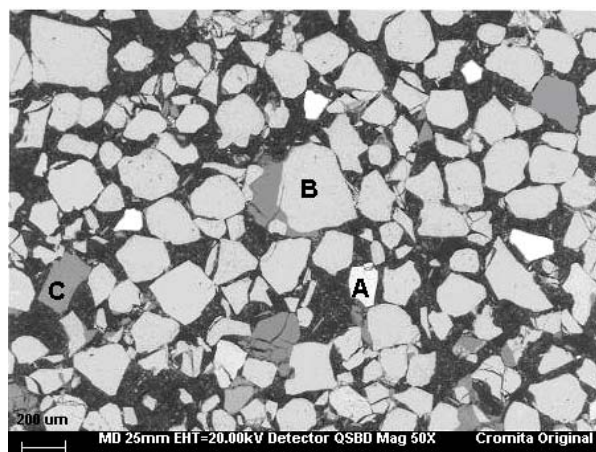


Figure 4. Scanning Electron Microscopy of the chromites showing three different components⁽⁹⁾

Table 4. Microanalysis (XEDS) of the particles show in the Fig 4⁽⁹⁾ (wt %)

	O	Mg	Al	Si	Ti	Cr	Fe
A	28.94	0.83	3.64		0.61	27.09	38.91
B	34.41	8.15	9.59	0.01	0.22	35.30	12.31
C	46.23	20.31	0.69	29.18	0.23	0.69	2.67

3 RESULTS AND DISCUSSIONS

The figure 5 (a) and (b) shows the pellets before and after the reduction, respectively, in the rotary kiln furnace (1773K, 30 min). The compression strength after reduction was 130 kgf/pellet.

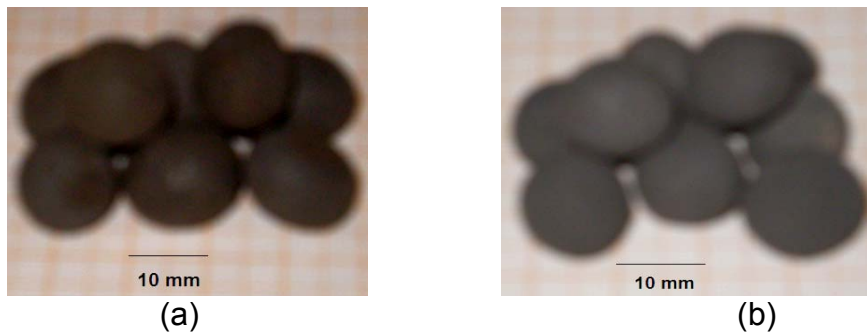


Figure 5. (a) Pellets before the reduction. (b) Pellets after the reduction (30 min at 1773K).

The reduction behavior along time, at 1773K at the reduction zone the furnace, for the pellets is presented in the Figure 6.

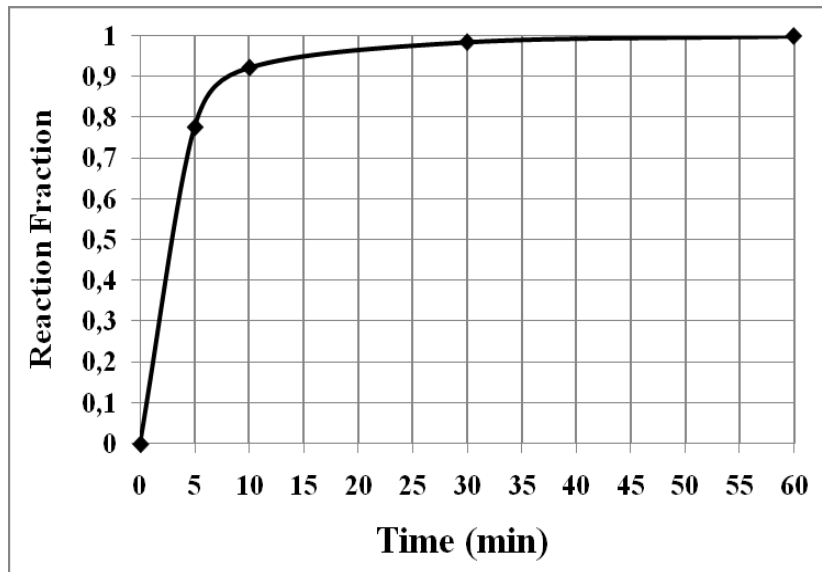


Figure 6. Reaction behaviors along time of pellets in the reduction zone of the laboratory kiln furnace.

Figure 6 shows the reduction evolution behavior when 200g, at each residence time, was charged. With this procedure it was observed that a reaction fraction reached ~87% within 7 minutes at 1773K. Almost complete reduction of chromite was observed after 30 minutes at 1773K.

The initial fast reaction rate (first 5 minutes) is credited to the mechanism of indirect solid/gas reduction and after this point a liquid phase (slag) start to form and then slower reduction rate is observed.

3.1 Micrographic Analysis

The micrographs of the reduced pellets are shown in figures 7-12. Figures 7 and 8 show, the reduced pellet during 5 minutes at 1773K, reaction fraction of 0.79 and with 200, 500 and 1000 magnifications, respectively.

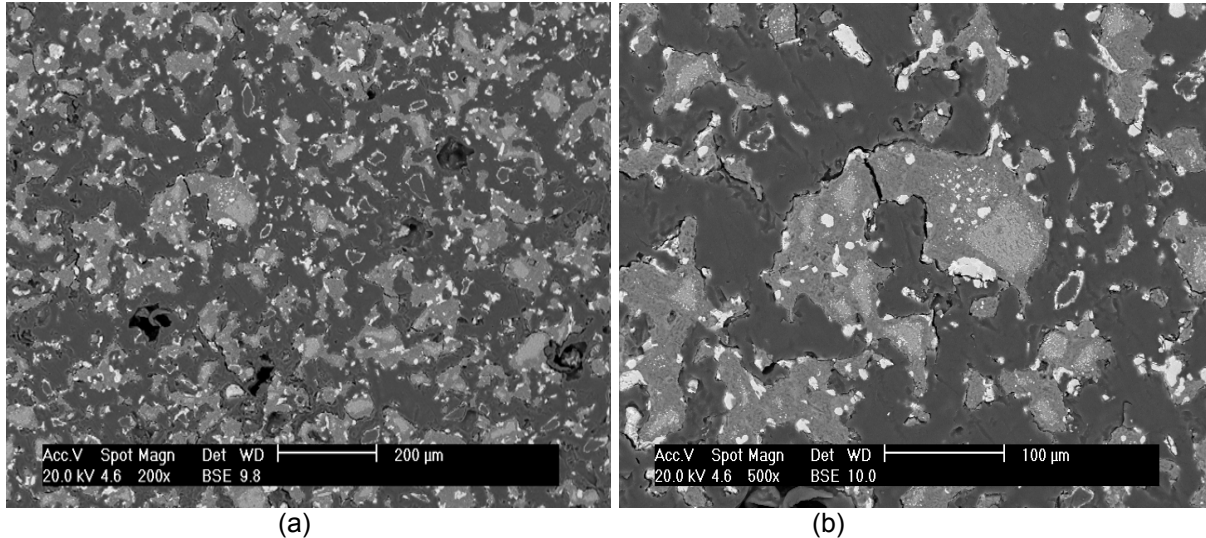


Figure 7. Scanning Electron Micrograph of reduced pellet, at 1773K (5 min), (a) 200X (b) 500 X. White metallic phase, dark grey continuous slag phase, grey chromite phase and black voids.

The Figure 8 and Table 5 show the white metallic phase with 55.78% Cr (spot 2, Figure 8), the particles of chromite without reduction/dissolution (spot 1, Figure 8) and some slag phase (spot 4, Figure 8). Large particles of chromites were only partially reduced and small particles were more reduced. The small particles dissolved forming a slag with some content of chromium (3%) and propitiated the coalescence of metallic particles. The temperature and time were not enough to dissolve the chromite to form the slag due to its refractoriness. The reduced pellet did not disaggregated and kept the spherical shape, with lot of porous (spot 5, Figure 8).

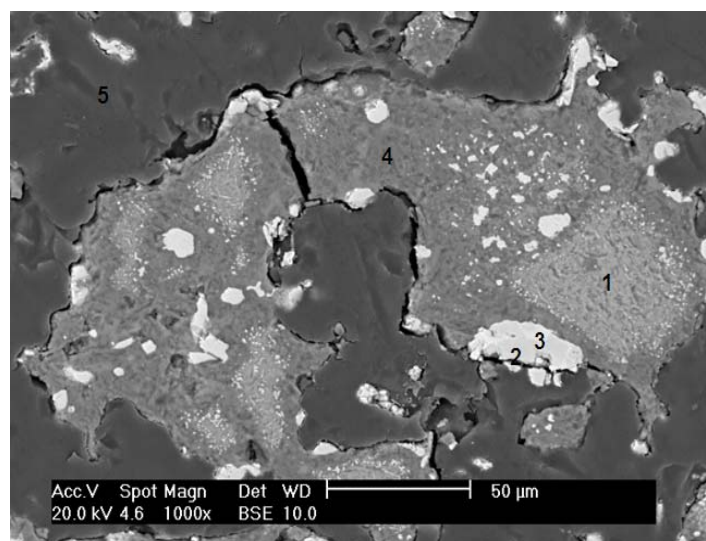


Figure 8. Scanning Electron Micrograph of pellet, at 1773K (5 min), 1000X. White metallic phase, dark grey continuous slag phase, grey chromite phase and black resin.

Table 5. Microanalysis (XEDS) of the phases in the pellet reduced during 5 minutes at 1773K. Figure 8. (wt%)

Phase	O	C	Mg	Al	Si	P	S	Ca	Cr	Fe
1	8.91	-	11.72	12.49	0.42	-	-	0.37	37.11	28.98
2	-	15.07	-	-	0.43	1.08	0.52	-	55.78	27.12
4	19.11	-	42.70?	0.86	31.31	-	-	1.92	3.06	1.06
5	Resin									

Figures 9 and 10 show the pellet with 10 minutes, reaction fraction of 0.92 with 200, 500 and 1000 magnifications, respectively.

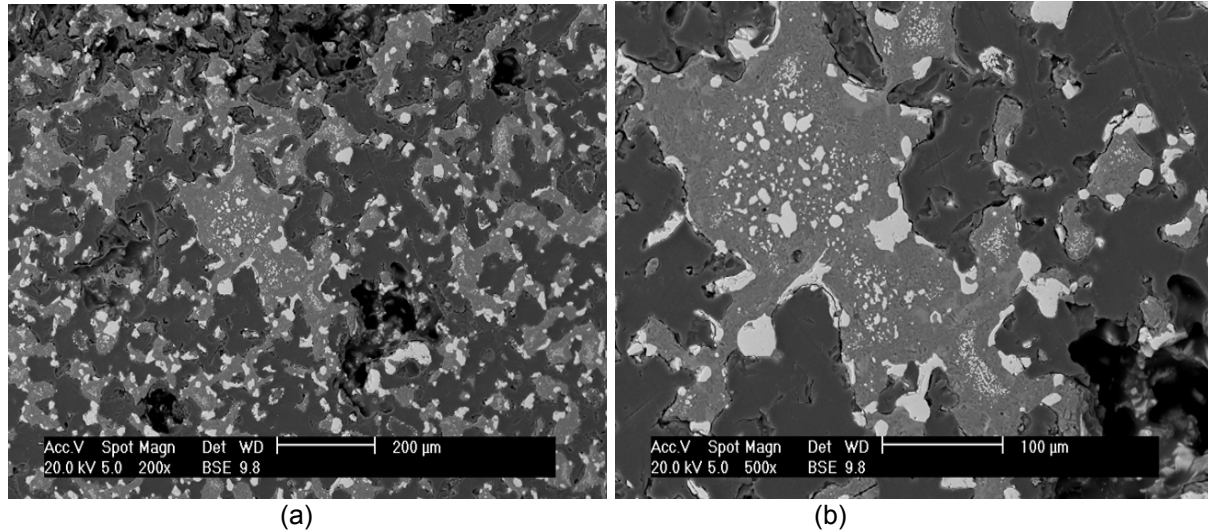


Figure 9. Scanning Electron Micrograph of pellet, at 1773K (10 min), (a) 200X, (b) 500 X. White metallic phase, dark grey continuous slag phase and black resin.

Figure 10 and Table 6 show the metallic particles with 62.02% Cr (spot 1, Figure 10), some formation of slag phase (spot 2, Figure 10) containing silicon, aluminum, magnesium, calcium oxides. At the temperature of 1773K during 10 minutes it is observed that almost complete reduction was occurred even for the large particles of chromite. The gangue from the large chromite particles did not dissolved completely to form slag and the coalescence of metallic phase was unfavorable. In comparison with residence time of 5 minutes (Figure 7a) and with of that of 10 minutes (Figure 9a) it is shown much more continuous slag phase interlinking the particles inside the reduced pellet.

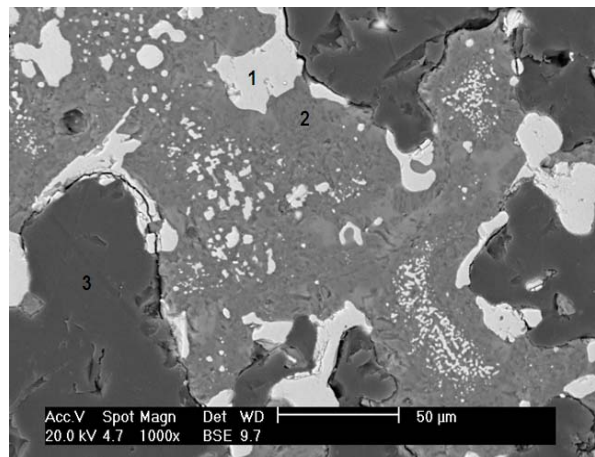


Figure 10. Scanning Electron Micrograph of pellet, at 1773K (10 min), 1000X. White metallic phase, dark grey continuous slag phase and black resin.

Table 6. Microanalysis (XEDS) of the phases in the pellet reduced during 10 minutes. At 1773K. Figure 10. (wt%)

Phase	O	C	Mg	Al	Si	P	S	Ca	Cr	Fe
1	-	10.62	-	-	0.51	0.78	0.09	-	62.02	25.98
2	12.98	-	9.43	10.92	28.94	-	-	35.26	1.30	1.16
3	Resin									

Figures 11 and 12 show the pellet with 30 minutes, reaction fraction of 0.98 with 200, 500 and 1000 magnifications, respectively. Figure 11 shows the continuous slag phase (gray), with metallic particles with good coalescence and no non dissolved residual chromite.

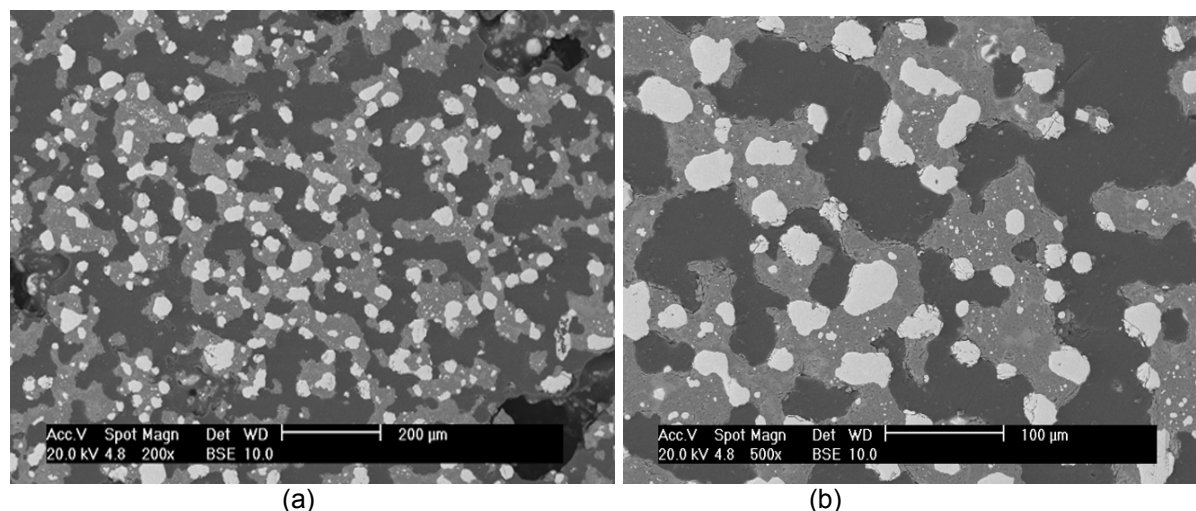


Figure 11. Scanning Electron Micrograph of reduced pellet, at 1773K (30 min). (a) 200 X, (b) 500 X. White metallic phase, dark grey continuous slag phase and black resin.

Figure 12 (1000X) and Table 7 show a metallic phase with 65.88% Cr (spot 1, Figure 12). The continuous slag phase (gray) contains calcium, silicon, magnesium, aluminum and small residual (0.8%) chromium oxides (spot 2, Table 7). A very porous reduced pellet with good compression strength (130 kgf/pellet) was obtained.

The metallic phase presented an excellent coalescence forming quite large particles. This coalescence did not improve with longer (60 minutes) residence time at 1773K (Figure 13).

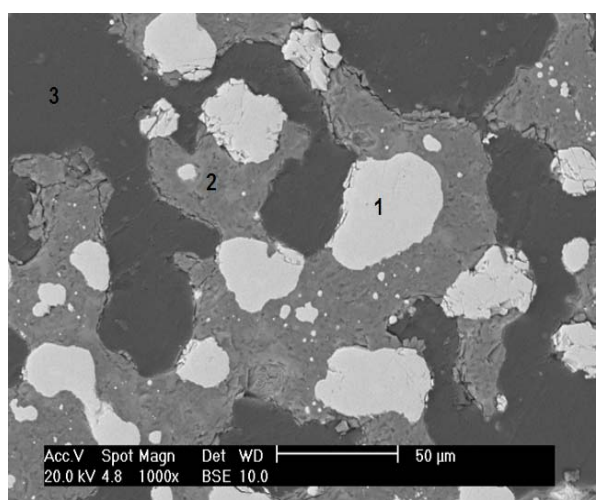


Figure 12. Scanning Electron Micrograph of pellet, at 1773K (30 min). 1000 X. White metallic phase, dark grey continuous slag phase and black resin.

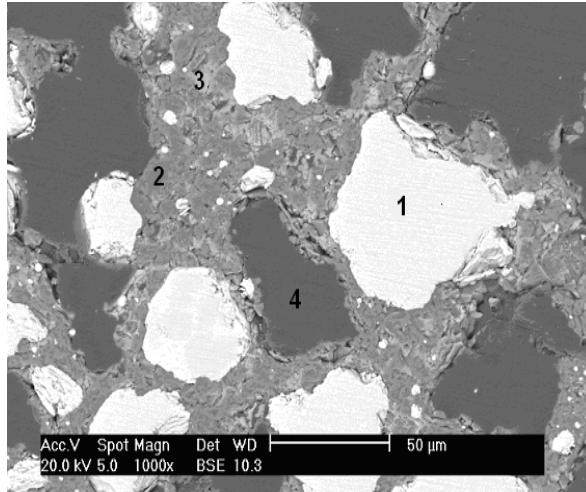


Figure 13. Scanning Electron Micrograph of pellet , at 1773K (60 min). 1000 X. White metallic phase, dark grey continuous slag phase and black resin.

Table 7. Microanalysis (XEDS) of the phases in the reduced pellet during 30 minutes at 1773K. Reaction fraction of 0.98. Figure 12. (wt%)

Phase	O	C	Mg	Al	Si	P	S	Ca	Cr	Fe
1	-	10.23	-	-	0.70	0.97	0.61	-	65.88	21.60
2	23.40	-	40.09	1.17	31.30	-	-	2.72	0.79	0.54
3	Resin									

The comparison of the results of pellets reduced during 5, 10 and 30 minutes at 1773K in the laboratory rotary kiln furnace (figures 8, 10 and 12; and tables V, VI and VII) shows chromium enrichment in the metallic phase and a decrease the chromium content in the slag.

Table 8 shows the chromium recovery between 93 and 98 with 5 and 30 minutes respectively.

Table 8. Chromium recovery for the different residence times in the laboratory rotary kiln furnace, at 1773K.

Residence time (min)	(XEDS) Microanalysis Cr	%CrO (XEDS)	Cr slag (g)	Cr Input (g)	Cr in alloy (g)	Chromium Recovery (%)
5	3.06	2.67	1,30	21.42	20.12	93.91
10	1.30	0.99	0.48	21.42	20.94	97.74
30	0.70	0.72	0.35	21.42	21.07	98.36

5 CONCLUSIONS

For experimental conditions used it can be concluded:

1. The metallic components recovery is high (98%), after 30 minutes at 1773K.
2. The micrographical evidence confirmed that almost complete reduction of chromite occurred after 30 minutes at 1773K.
3. A slag phase starts to form at 5 minutes at 1773K but not continuously.
4. The reduced pellet at 30 minutes is porous, with formation of continuous slag phase, but the pellet kept the original form.

5. This coalescence did not improve with longer (60 minutes) residence time at 1773K.
6. The reduced pellet presented compression strength of the 130 kgf after 30 minutes at 1773K and re-oxidation was not observed.
7. The results show a great potential for using self-reducing pellets of chromite to produce high carbon ferro-chromium (HCFerCr).

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