RESEARCH ON THE FERROCHROMIUM COALESCENCE IN SELF-REDUCING PELLETS [1]

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Abstract

Efficient process has been developed for production of ferrochromium (FeCr) by the use of chromium ore fines in self-reducing agglomerates. It increases reaction rates and decreases the energy consumption, therefore reducing its final production cost. The reduction process of pellets composed of chromium ore, cement, CMC, petroleum coke and Fe-Si was studied. Two different particles size of chromite were used: -400# (d<38µm) and -50#+65# (210µm<d<300µm). The experiments were carried out at 1773K. The global reduction mechanism follows: 1) chromite reduction by gas/solid reaction; 2) as the reaction takes place, the initial slag begins to melt, dissolving the ore; 3) The gas/solid reaction is progressively replaced by the slag/carbon and metal/slag reaction. The coalescence mechanism was different for the two types of pellet. In the -400#, it was obtained a more homogenous coalescence (final metal particles with similar size). For the -50#+65#pellet, it was obtained bigger metal particles, however with large amount of small particles, without coalescence.

Key words: Chromite; Particle size ore; Self-reducing agglomerate; Ferrochromium; Coalescence.

ESTUDO DO COALESCIMENTO DE FERRO-CROMO EM PELOTAS AUTO-REDUTORAS

Resumo

O uso de finos de minério de cromo na forma de aglomerados auto-redutores tem se mostrado eficiente, uma vez que aumenta a velocidade de redução e diminui as demandas energéticas, reduzindo os custos finais do processo. Neste trabalho estudou-se o comportamento de redução de pelotas compostas de minério de cromo, cimento, CMC, coque de petróleo e Fe-Si. Utilizou-se minério de cromo em duas diferentes granulometrias: -400# (d<38µm) e -50#+65# (210µm<d<300µm). O mecanismo de redução global é: 1) redução da cromita por reação gás/sólido, 2) em conjunto com essa redução, a escória inicial começa a se formar e o minério a se dissolver, 3) a reação gás/sólido dá lugar à reação escória/carbono e metal/escória. O mecanismo de coalescimento foi diferente para os dois tipos de pelotas. Na -400# obteve-se um coalescimento mais homogêneo (partículas finais de metal com tamanho similar), na -50#+65#, maiores partículas de metal foram obtidas, mas com muitas partículas ainda não coalescidas.

Palavras-chave: Cromita; Granulometria; Aglomerado auto-redutor; Ferro-cromo; Coalescimento.

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1 INTRODUCTION

The chromium ore is essentially composed of free iron oxide, $FeO.Cr_2O_3$, $MgO.Cr_2O_3$, $MgO.Al_2O_3$, $(Cr,Al)_2O_3$ and a magnesium silicate, forming a complex solid state spinel structure.(1) This ore is conventionally processed in smelting electric arc furnace, where it is dissolved in the initial slag and this enriched on Cr slag is reduced by the carbon floating on the bath and by the carbon dissolved in the metal phase.

The gangue of the chromium ore is composed by refractory oxides (basically MgO & Al_2O_3), therefore high energy consumption is incurred to keep this process on stream. Other problem is the slag (liquid)/carbon (solid) reaction that is slow and depends on the bath surface in contact with the reductant.

One alternative route to reduce the energy consumption and to make it a faster process is the use of self-reducing agglomerates. This is due to the gas/solid reaction, between the chromite and the CO from the Boudouard reaction. After the reduction reaction, the gangue of the ore is dissolved into a primary slag and the metal particles are free for coalescence.

The aiming of this work is to verify the influence of the chromium ore particle size in the reduction behavior and metal coalescence in self-reducing pellets.

1.1 Thermodynamics Analysis Of Chromite Reduction

A detailed thermodynamics analysis can be found in papers already presented by the authors. (2-4)

The oxides reduced in the experiments carried out are the iron and chromium oxides. The minimum reduction temperature of these oxides is function of the products activities and with the $FeO.Cr_2O_3$ activity in the ore.

Hino et al(1) evaluated the $FeO.Cr_2O_3$ activity with a complex solid structure of the type - $FeO.Cr_2O_3$ - $MgO.Cr_2O_3$ – $MgO.Al_2O_3$ also with presence of $(Cr,Al)_2O_3$. The authors observed a negative deviation of ideality, being the $FeO.Cr_2O_3$ activity around 0.183 at 1473K and around 0.173 at 1773K.

The reduction reactions of the chromium ore are shown in Table 1, with the temperature required for the starting of the reaction. There are two columns, one for $FeO.Cr_2O_3$ activity being 1 and other for 0.155. The products activity was considered one, at the same pCO/pCO_2 rate.

Table 1.Minimum temperature for the chromite reduction reactions occur.

Reactions		T(°C) a($FeO.Cr_2O_3$)=1	T(°C) a($FeO.Cr_2O_3$)=0,155
1	<FeO> + (CO) = <Fe> + (CO_2)	691	691
2	<$FeO.Cr_2O_3$> + (CO) = <Fe> + <Cr_2O_3> + (CO2)	1124	1276
3	<$FeO.Cr_2O_3$> + 4(CO) = <Fe> + 2<Cr> + 4(CO_2)	1303	1341
4	7<$FeO.Cr_2O_3$> + 40(CO) = 7<Fe> + 2<Cr_7C_3> + 34(CO_2)	1239	1306
5	3<$FeO.Cr_2O_3$> + 20(CO) = 3<Fe> + 2<Cr_3C_2> + 16(CO_2)	1237	1253
6	3<$FeO.Cr_2O_3$> + 5(CO) = <Fe_3C> + 3<Cr_2O_3> + 4(CO_2)	1157	1308
7	<Cr_2O_3> + 3(CO) = 2<Cr> + 3(CO_2)	1360	1360

<_>:solid, (_): gas

1.2 The Influence of Slag Composition on The Reduction Behavior

According to Jansson et al.,(5) the slag has an important role on the ferrochromium production, because the process is a combination of solid state reduction and ore dissolution into the slag. The reduction rate can vary with the *liquidus* temperature of the slag, depending on the acting mechanism. Takano et al.(3) has already reported it. They observed, in self-reducing chromite pellets, that the chromite reduction is faster when the slag forms later. This is due to the reduction mechanism. Before the slag formation, the reduction is through the gas/solid and solid/solid reactions. After the slag formation, the CrO_x has to dissolve into the liquid slag, and the reaction occurs between the carbon floating on the slag and the CrO_x contained in the slag phase (solid/liquid reaction), or through the reaction between the carbon dissolved in the metal and the CrO_x contained in the slag (liquid/liquid reaction, controlled by diffusion). These two mechanisms are slower than the solid/gas reaction.

1.3 The Influence of Chromite Particle Size on The Reduction Behavior

The chromite reduction rate in solid state depends heavily on its particle size,(6,7) as shown in Figure 1.

According to Beneduce(4) the chromite reduction begins with the iron reduction in the outer layer of the ore particle, at the same time the diffusion of Fe atoms to the core and the Cr atoms to the outer layer occur. So, smaller the ore particle easier is the reduction, because the ore has higher specific area and the diffusion distance is shorter.

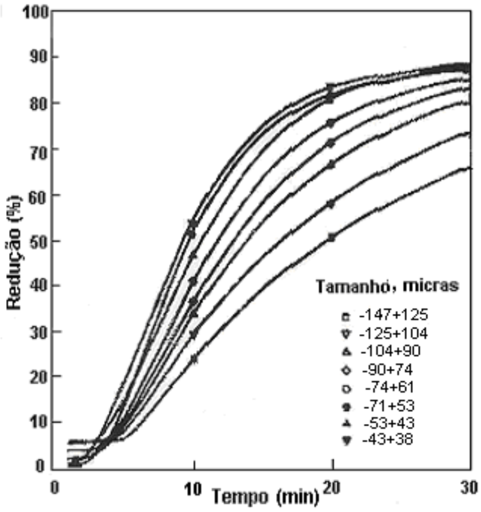

Figure 1. The chromite particle size effect in the reduction velocity of the self-reducing pellets of South-African chromite – LG6 at 1689K.(7)

1.4 Energy Necessary For Reduction And Melting

The production process of ferrochromium, by using the self-reducing pellets, can be divided in two steps: reduction at 1773K and melting at 2073K. The mass balance and the energy balance are shown in Table 2.

Table 2: Mass and energy balance for reduction, at 1773K, and melting, at 2073K, self-reducing pellets of chromite.

Mass balance			Energy Balance			
	In (kg)	Out (kg)	Reduction	kWh	Melting	kWh
Chromite	760	-	Heat up	800	Heat up	452
Petroleum Coke	170	-	Reaction	227	Reaction	0
Cement	5	-	Energy loss (%)	15	Energy loss (%)	15
Metal (60% Cr)	-	330	Total	1.027	Total	452
Slag	-	363	Total (consid. loss)	1,147	Total (consid. loss)	520
TOTAL	935	693	TOTAL (no melting)	1,147	TOTAL (with melting)	1,667
			Saved Energy (kWh)	520		
			Saved Energy (%)	30		

The major part of the energy is used in the reduction step (69%), because carbothermic reduction is an endothermic reaction and high temperature is needed to achieve a high reduction rate.

The melting step uses around 30% of the total required energy.

2 MATERIALS AND METHODS

The pellets were made with Brazilian chromium ore in two different particles sizes: coarse, -50#+65# (210μm<d<300μm); and fine, -400# (d<37μm); Portland cement; Fe-75%Si; petroleum coke; CMC (CarboxyMethyl Cellulose). The chemical composition and particle size distribution of these raw materials are shown in Table 3 and Table 4, respectively.

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

Component	Chromite	Petroleum Coke	Portland Cement	Fe-Si
Cr_2O_3	41.2			
Fe_2O_3	-		2.8	
FeO	16.9			
SiO_2	5.7		19.1	
Al_2O_3	17.3		4.9	
MgO	15.6		0.3	
CaO	0.4		64.3	
CaO free			1.0	
CO_2	-			
Vol. Matters	-	10.8		
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			2.6	
K_2O			0.7	
Na_2O			0.04	
Others			4.0	

Table 4. Particle size distribution of the raw materials (% accumulated).

Sieve (#)	(μm)	Petroleum Coke	Cement	Fe-Si
100	147	100		100
150	104		100	80.8
200	74			26.0
270	53			4.0
400	38			1.4

The electron micrograph of the chromite is shown in Figure 2. Microanalysis (XEDS) of different phases was carried out, and the results are shown in Table 5.

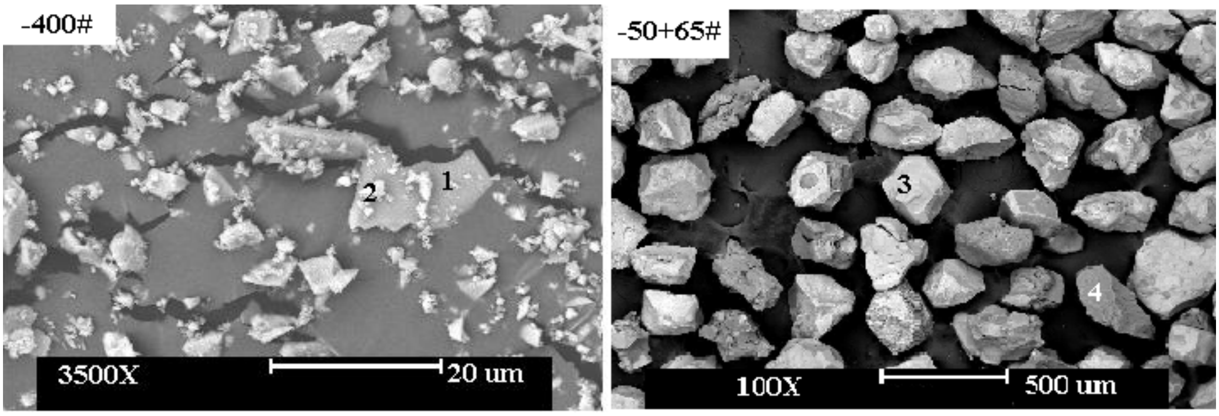

Figure 2: Chromite (Jacurici concentrate) micrograph. (1), (2) and (3) are chromite particles and (4) is the gangue containing SiO_2, MgO and CaO.

Table 5: Microanalysis (XEDS) of different phases in the chromite (Jacurici concentrate). (wt %).

Phase	O	Mg	Al	Si	Ca	Ti	Cr	Fe
1	13,6	11,4	12,6	0,8	0,3	0,6	43,0	17,6
2	23,9	14,6	14,5	2,5	0,2	0,08	31,2	13,1
3	21,1	11,3	12,0	0,8	0,2	0,09	36,7	17,9
4	21,6	22,1	0,7	34,8	10,3	-	1,8	8,8

After dried, the raw materials were mixed in a Turbula mixer. The pellets were handmade.

The chemical composition of pellets is shown in Table 6.

The C-content was enough to reduce all chromium and iron oxides plus 20% in excess.

The pellets were dried and then submitted to reduction tests, using the special system heated by induction furnace (shown in Figure 3) and with argon flow of 2L/min.

Table 6. Composition of the handmade pellets. (wt %)

	Particle size	
Component / pellet	-50#+65#	-400#
Chromite	75,59	76,00
Petroleum coke (20% excess)	16,89	17,00
Fe-Si (75% Si)	2,00	2,00
Portland Cement	5,03	5,00
CMC	0,50	0,00
Total	100,00	100,00

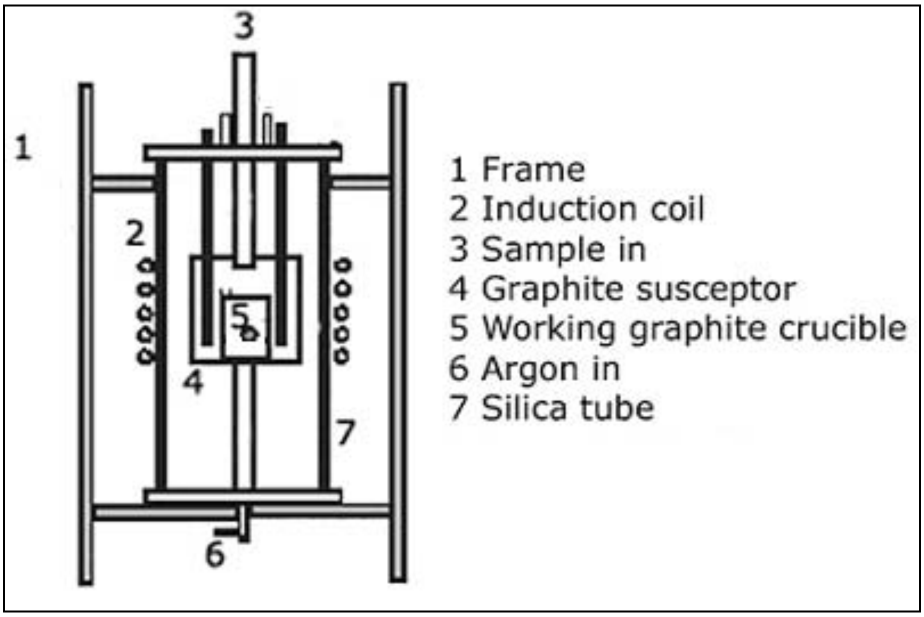

Figure 3. System used for the reduction experiments.

The cold pellets were placed directly into the pre-heated graphite crucible and stabilized at 1773K. The cooling down to room temperature was made also with argon flow, following the temperature profile shown in Figure 4.

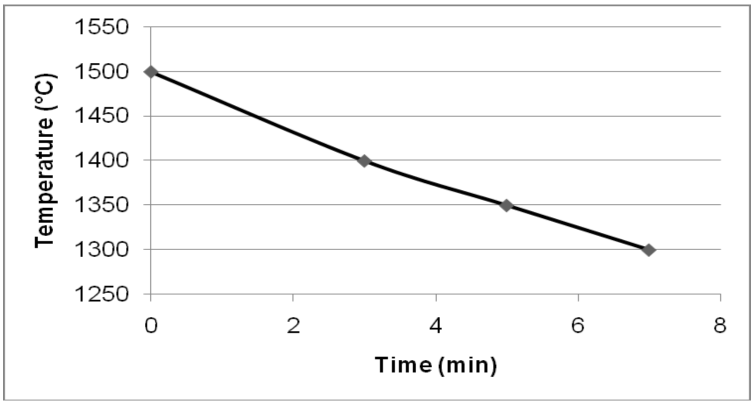

Figure 4. Cooling down temperature profile.

3 RESULTS AND DISCUSSION

Figure 5 shows the reaction fraction as function of the time for the pellets -50#+65# and -400# at 1773K. The reaction fraction was calculated with the Cr-content in the slag measured by XEDS. The reaction rate for these two types of pellets was high due to the Si-reduction of Cr-oxides, which are exothermic reaction.(2) The -400# pellet presented the fastest reduction, as shown in Figure 5.

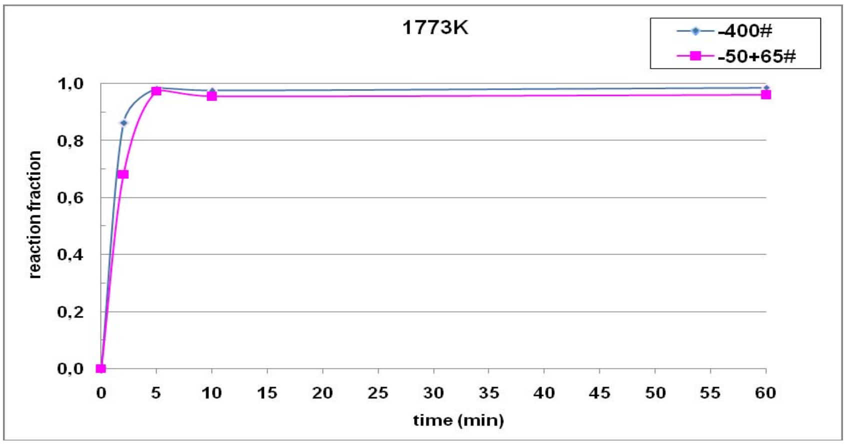

Figure 5. Reaction behaviors along time, of -50#+65# and -400# pellets at 1773K.

Both types of pellets (fine and coarse ore) follow the same reduction mechanism. If there is some free FeO, the reduction starts at ~973K. The initial reduction temperature of the $FeO.Cr_2O_3$ is ~ 1473K. The chromite is partially reduced by the direct reaction between carbon and ore particles and, mainly, by the gas/solid reaction between the CO generated from the coke gasification reaction (Boudouard reaction) and the ore particle. The liquid phase formation should start at around 1673K.(3).

Below this temperature, the chromite reduction reaction rate is low.(4) The liquid phase, named initial slag, is composed by cement, part of the ore gangue and the coke ash. After the initial slag formation, the ore starts to dissolve into this slag. So the reduction by the gas/solid reaction is replaced by slag/carbon and metal/slag reactions that have a lower reduction rate, when compared, at the same temperature, with the gas/solid and solid/solid reaction.

Concisely, the mechanism follow three steps: 1) chromite reduction by gas/solid reaction; 2) as the reaction takes place, the initial slag begins to form, dissolving the ore in it; 3) The gas/solid reaction is replaced by the slag/carbon and metal/slag reaction.

Figures 6 to 9 show the electron micrograph of the pellets submitted to reduction experiments.

Figure 6 shows the pellets after 2 minutes of reaction. The chemical analysis of different phases of these pellets is shown in Table 7.

For the -400# pellet, some ore is dissolved into the primary slag (phase 1, which shows high Al_2O_3 and MgO content with some Cr-content). The resultant slag has high viscosity, so the metal coalescence is a difficult process. That is why the metals particles are not well coalesced, and they are entrapped in the slag (phase 1) as small particles.

The presence of metal involving the carbon particles is the evidence that the slag/carbon reaction is occurring (phase 2). The carbon particles are enveloped by the slag, so it is difficult the CO production to reduce the ore and the slag enriched in Cr-oxide.

For the -50#+65# pellets it is possible to see the presence of the slag (phase 4) among the partially reduced chromite particles (phase 5). The dissolution of the chromite particles is slower than in pellet with fine ore due to the lower specific area and coarser particle size. This conclusion can be achieved by the chemical analysis of Phase 4, which shows lower amount of Al_2O_3, MgO and Cr_2O_3 in comparison to Phase 1.

This lower dissolution produces a slag with lower viscosity. So it is easier to the free metallic particles to coalesce. That is why it can be seen a metal particle with ~70 μm.

For both cases it is possible to see metallic particles entrapped in the slag. They are the result of gas/solid reaction that happened before the initial slag formation.

The gas/solid reaction occurs during a longer period of time in the -50#+65# pellets, but due to the bigger particles size the reduction rate is lower (at 2 minutes the reaction fraction of the coarse particles was ~65% and for the fine one was ~85%).

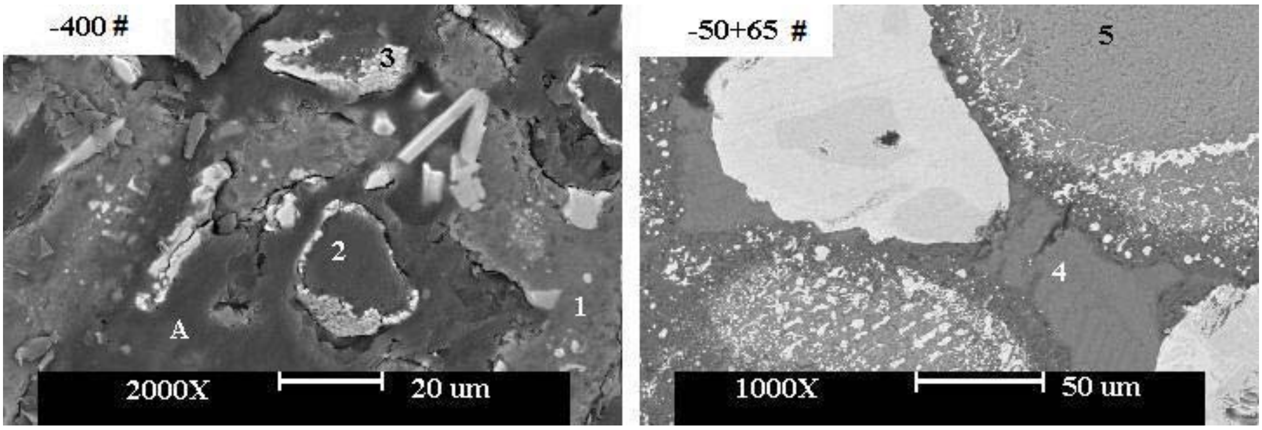

Figure 6. Electron micrographs of the pellets after 2 minutes at 1773K. Formed slag (phase 1); carbon particle entrapped in the slag (phase 2); formed metal in the slag/carbon interface (phase 3); formed slag (phase 4); partially reduced chromite (phase 5).

Table 7: Composition of different phases in the reduced pellets at 1773K after 2 minutes.

Phase	C	O	Mg	Al	Si	Ca	Cr	Fe
1		17.97	21.99	24.87	19.33	9.96	4.49	1.39
2	100							
3	8.00				0.44		64.39	27.17
4		19.00	7.24	11.08	28.77	32.44	0.66	0.8
5		14.19	11.97	15.97	0.63	0.37	40.33	16.64
A	Resin							

The Figures 7 to 9 show the reaction progress, which occurred through the solid/liquid reaction.

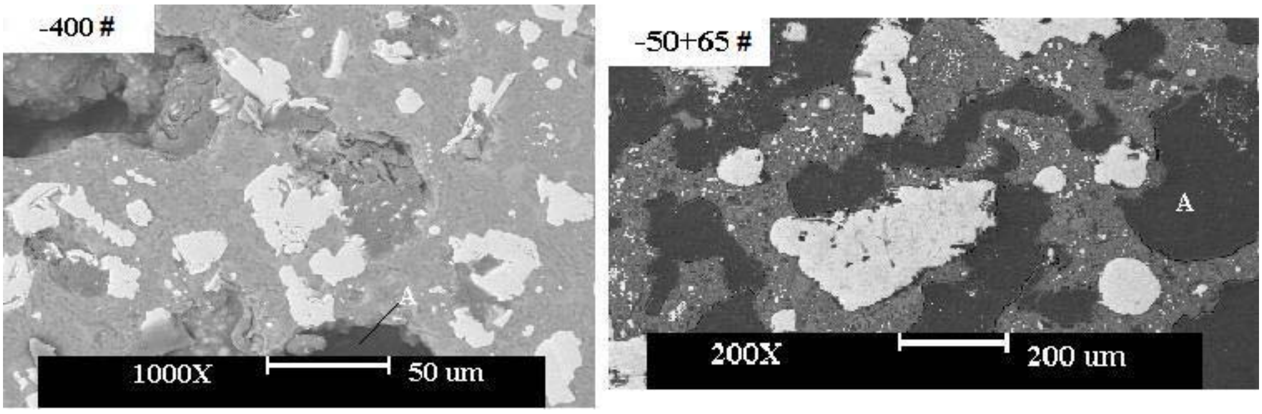

Figure 7. Electron micrographs of the pellets after 5 minutes at 1773K.

The Figure 7 shows that the coalescence process proceeds with time – coarser metal phases are observed, in comparison with Figure 6. For the -50#+65# pellets, it was observed some chromite dissolution and a continuous slag phase was observed.

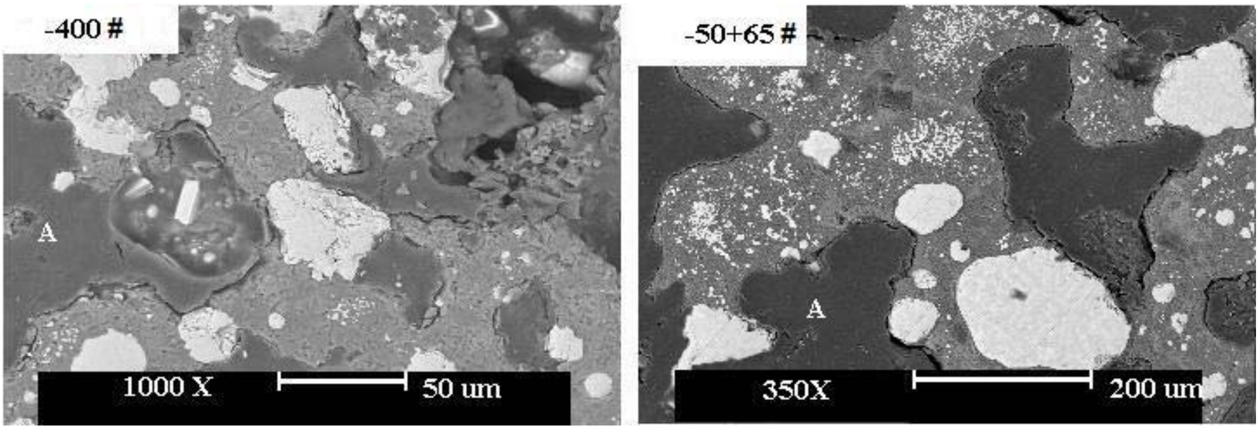

Figure 8. Electron micrographs of the pellets after 10 minutes at 1773K.

In Figure 8, the same phases were observed.

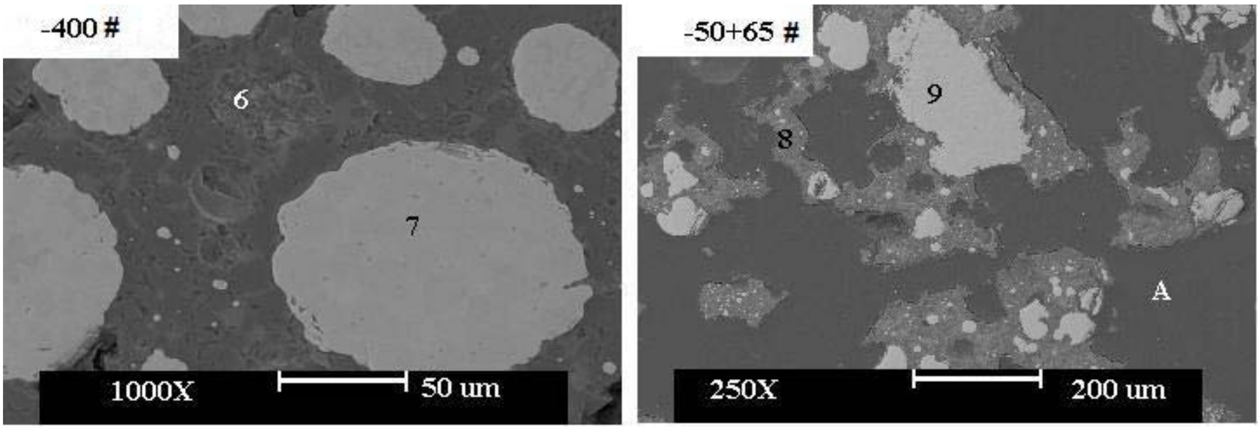

Figure 9. Electron micrographs of the pellets after 60 minutes at 1773K.

The metal is well coalesced (phases 7 and 9), although there are still some metallic particles entrapped in the slag (phases 6 and 8).

The coalescence mechanism is different for the two types of pellets. For the fine ore, the metal coalescence is slow all the time, because the dissolution of the ore is fast, so the slag becomes viscous. As the result, the formed metal is free to coalesce from the beginning, however at low speed.

For the -50#+65# pellet, the metal coalescence is faster in the beginning (less viscous slag in this step) but as the chromite ores dissolve in the primary slag, the coalescence speed starts to decrease due to increase in viscosity.

After 10 minutes of reaction (Figure 7), in the -50#+65# pellet, there are metal particles with more than 200μm, and for the -400# pellet the metal particles are smaller than 50μm. After 60 minutes (figure 9), the bigger metal particles are in the -50#+65# pellet, but there are more non-coalesced metals; in the -400# pellet the particles are more spherical and there is less non-coalesced metals.

As the metal was first free to coalesce in the -400# pellet, it was obtained a more homogenous coalescence. For the -50#+65# pellet, it was obtained large metal particles, but there were many non-coalesced metal particles.

Table 8 shows the composition of the different phases in the pellets after 60 minutes of reduction.

Table 8. Composition of different phases in the reduced pellets at 1773K after 60 minutes.

Phase	C	O	Mg	Al	Si	Ca	Cr	Fe
6		19.37	18.81	35.97	15.43	8.89	0.88	0.65
7	7.99				4.97		52.24	34.8
8		21.64	13.82	33.34	10.10	17.70	2.24	1.17
9	6.26				9.06		54.91	29.77
A	Resin							

The slag composition shows that the Phase 6 (fine ore) still has higher Mg & Al-oxide than Phase 8, after 60 minutes at 1773K.

4 CONCLUSIONS

For the experimental conditions used in this study, the conclusions are:

a) In a self-reducing pellet composed by chromium ore, reductants, and cement, it was confirmed that the reduction mechanism of the pellet occurs mainly by: 1) chromite reduction by gas/solid reaction; 2) as the reaction takes place, the initial slag begins to form. This slag is composed by the cement, the coke ash, and some ore (fines, less than 38μm, are dissolved in the first liquid); 3) The gas/solid reaction is substituted by slag/carbon and metal/slag reaction.

b) The reduction rate was high for both types of pellet. The -400# pellet showed higher reduction rate than the -50#+60# pellet.

c) After 2 minutes of reduction, the amount of chromite dissolved in the initial slag is higher in pellet made with fine ore than with coarse ore. After 60 minutes, the Al-content and Mg-content was still higher for the pellet made with fine ore.

d) As the metal was first free to coalesce in the -400# pellet, it was obtained a more homogenous coalescence (final metal particles with similar size), and less non-coalesced metal dispersed in the slag.

e) For the -50#+65# pellet, it was obtained bigger final metal particles, but there were many non-coalesced metal particles dispersed in the slag.

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