INFACON 7, Trondheim, Norway, June 1995
Eds.: Tuset, Tveit and Page
Publishers: FFF, Trondheim, Norway

KINETICS OF CHROMITE DISSOLUTION IN LIQUID SLAGS

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ABSTRACT

The dissolution behaviour of chromite in SiO_2-Al_2O_3-MgO-CaO slags is being studied in the temperature range of 1535°C and 1700°C. Rotating cylinder technique is used, where chromite cylinders are immersed in the slag phase and data for the rate of dissolution is obtained by sampling the slags at predetermined intervals. Experiments have been designed by a statistical procedure.

The experimental work conducted hitherto showed that the dissolution of chromite in the slag contained in graphite crucibles at 1535°C is very rapid and takes place concurrent with the reduction of dissolved chromite on the crucible walls. The experimental work, X-ray and scanning Electron Microscopy (SEM) studies on the reacted samples continues.

INTRODUCTION

For addition to ferrous alloys, chromium is usually produced as a ferro-chromium alloy containing approximately up to 70 per cent chromium [1]. Ferro-chromium is currently produced by the smelting of chromite in submerged-arc electric furnaces. The chromium recovery in the production is mainly determined by the chromium content of the discard slags. In the previous studies it was proven that the chromium losses to slag occur mainly in the form of metal drops and small particles of ore, and chromium recovery always depends on the melting behaviour and the reducibility of the ore [2-7,8].

From a kinetic point of view, the present investigation aims at understanding the mechanism of chrome ore dissolution in the slag systems encountered in the ferro-chromium production to help increase the chromium recovery for a more cost effective production strategy. The effects of slag composition, time, temperature and rotational speed (under reducing and neutral conditions) are investigated on the basis of statistical designing of the experiments. Ongoing experimental work including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray-diffraction and metallographic analyses is being carried out on the reacted samples to elucidate the effect of each parameter, and to establish the reaction mechanism.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Details of the equipment and experimental procedure are given below.

Induction Furnace and the Reaction Chamber

The heating unit is a stable 50 kW, 3 kHz induction furnace. The reaction chamber (Figure 1) consists of a fused silica tube 500 mm long, with an external diameter of 120 mm and an internal diameter of 114 mm. The lower end of the tube is closed. The top end is closed by a water cooled brass plate, with an O-ring between the silica tube and the brass plate to ensure gas tightness. A dense graphite crucible is used as the heating element. Another graphite crucible with a length of 80 mm and an internal diameter of 47 mm, containing the charged melt is placed within the heating element. A graphite cover is used as a radiation shield. The space between the heating element and silica tube, as well as the bottom part of the silica tube is packed with lampblack for insulation.

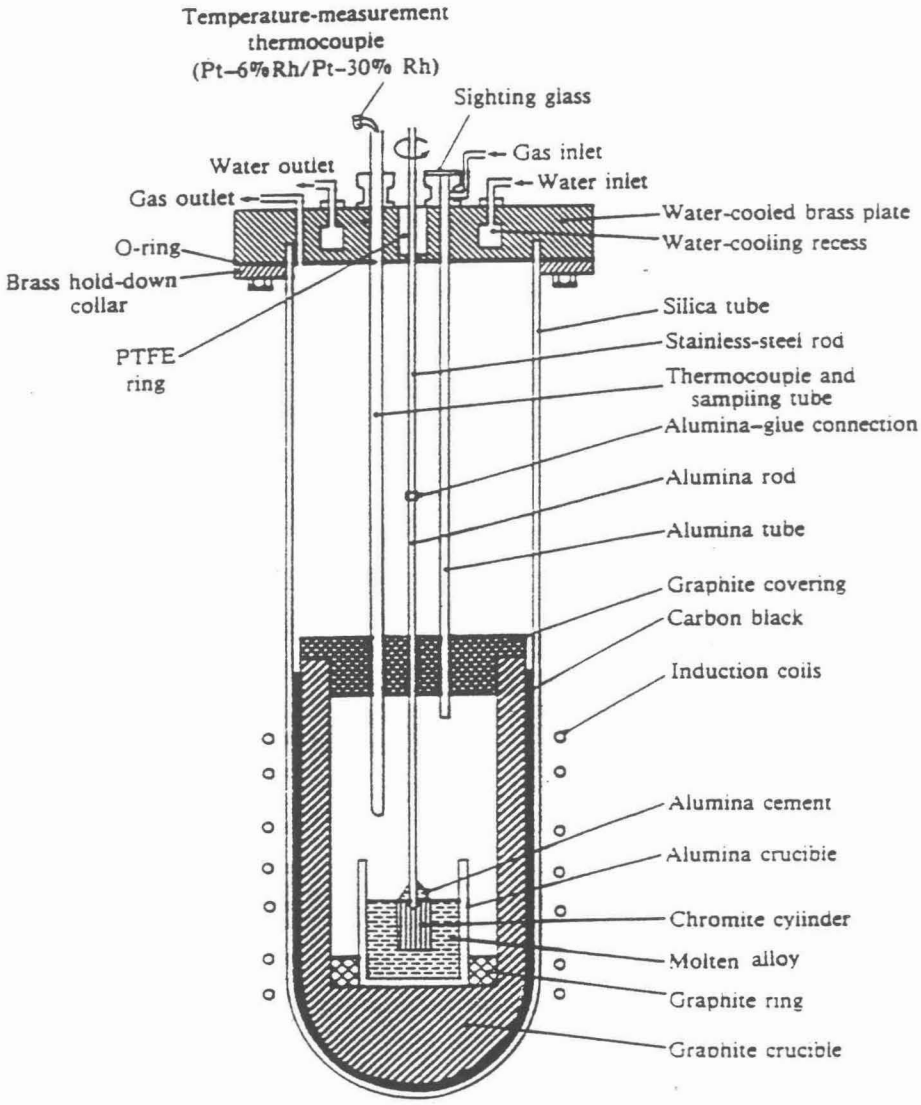

Fig. 1. Schematic representation of the reaction chamber. Power unit is a 50 kW, 3kHz induction furnace.

A type B (Pt-6% / Pt-30% Rh) thermocouple is used for temperature measurements. The furnace assembly is gas tight, during the experiments the pressure in the system is slightly above the ambient pressure. The system is flushed by dried and deoxidized high impurity argon gas. The flowrate of the gas which is measured by a capillary flowmeter is 2200 cm^3/min. Before it entered the system the gas is dried in a drying chamber filled with anhydrous $Mg(ClO_4)_2$ as a desiccant, as well as silica gel. The gas then enters a furnace containing copper chips which is maintained at 500°C for deoxidation. The gas is then introduced into the reaction chamber through a junction to an alumina inlet tube with an inner diameter of 5 mm. The lower end of the inlet tube is located 15 cm above the surface of the melt, while the top end is closed by a sighting glass throuhg which the interior of the reaction chamber can be observed.

Production of Chromite Spinel Cylinders

The chromite cylinders were prepared from tabled and pulverized LG-6 chromite powders. After pulverization, the powder was formed into dry cylinders without binders, by uniaxial pressing in a steel mould under a pressure of 6 t. The final dimensions of the cylinder are 15.6 mm in diameter and 18-20 mm in length, and it's mass changes between 13 and 15 grams. This was followed by sintering under argon at a flowrate of 2200 cm^3 /min, at 1450°C for 3 hours. Cylinders which had any crack after the sintering operation were rejected. The chemical analysis of the as received, pulverized and sintered chromite are given in Table I.

Table I: Chemical analysis of the as-received, pulverised and sintered chromite.

	Component, Mass %						
Chromite	Fe_2O_3	Cr_2O_3	Al_2O_3	SiO_2	TiO_2	MgO	CaO
As Received	23.1	49.3	12.8	2.60	0.42	10.9	<0.20
Pulverised	24.2	49.7	12.9	2.89	0.43	10.8	0.19
Sintered	24.3	49.8	12.1	2.82	0.41	10.8	0.20

Slag Compositions

There are a few equilibrium studies completed previously on the chromite dissolution in liquid slag systems similar to the slags involved in the present investigation. In these studies the slag composition ranges were very narrow compared to this study. Although in the actual process slags contain certain amounts of chromium and iron oxides, they were excluded from the slag composition in the present investigation. Because much of the chromium present in the slag is in the form of undissolved ore, partially reduced ore or alloy prills which will not affect the properties of the slag and in the real production situations in a good operation the amount of chromium and iron oxides dissolved in the slag is low. Also the valence state of the chromium in the slag is not known; in the divalent stage chromium will act as a modifying cation but in the trivalent state chromium will behave as a network former. Finally decreasing the number of components will simplify the system [3].

The slag compositions employed in this study were in the range of: 35-50% SiO_2, 5-30% Al_2O_3, 5-30% MgO, 5-35% CaO. The experiments were conducted according to statistical designing, the compositions of the slags determined by the mixture design are given in Table II. In this design the factor space created by the lower and upper boundary constraints of each component (eg SiO_2, Al_2O_3, MgO, CaO) represents a complex polyhedron. The slag compositions in each particular experiment are the points on the verices, face centorids and overall centroid of this geometrical shape.

Table II: Coordinates of the 20 design points for the slag compositions in the defined constraints (SiO_2: 35-50%, Al_2O_3: 5-30%, MgO: 5-30%, CaO: 5-35%).

Mixture Component Proportions (Coordinates), Mass % / 100							
Design point	Type of Boundary	SiO_2	Al_2O_3	MgO	CaO	Combination of vertices	Melt. P, °C
I	Vertex	0.35	0.30	0.05	0.30		1380
II	Vertex	0.35	0.30	0.30	0.05		1690
III	Vertex	0.35	0.05	0.30	0.30		1750
IV	Vertex	0.50	0.05	0.30	0.15		1520
V	Vertex	0.50	0.30	0.05	0.15		1380
VI	Vertex	0.35	0.05	0.25	0.35		1700
VII	Vertex	0.50	0.05	0.10	0.35		1390
VIII	Vertex	0.50	0.30	0.15	0.05		1430
IX	Vertex	0.35	0.25	0.05	0.35		1415
X	Vertex	0.50	0.15	0.30	0.05		1520
XI	Vertex	0.50	0.10	0.05	0.35		1400
XII	F / C*	0.35	0.19	0.19	0.27	1,2,3,6,9	1520
XIII	F / C	0.50	0.16	0.16	0.18	4,5,7,8,10-1	1320
XIV	F / C	0.42	0.30	0.14	0.14	1,2,5,8	1530
XV	F / C	0.42	0.05	0.24	0.29	3,4,6,7	1415
XVI	F / C	0.42	0.14	0.30	0.14	2,3,4,10	1570
XVII	F / C	0.42	0.24	0.05	0.29	1,5,9,11	1380
XVIII	F / C	0.45	0.25	0.25	0.05	2,8,10	1490
XIX	F / C	0.43	0.11	0.11	0.35	6,7,9,11	1360
XX	O / C*	0.43	0.17	0.17	0.22	1,2,3,4,....,11	1360

* F / C: Face Centroid, O / C: Overall Centroid

Master slags were prepared from chemically pure components. SiO_2, Al_2O_3, MgO and CaO powders were mixed at appropriate proportions. The homogeneous mixtures were then melted in a graphite crucible in the unduction furnace to provide a better homogenization. The molten slag was then poured into cast iron moulds for solidification. The solid slag samples were finally ground to powder form by the sieb technique. During the experiments the required composition was obtained by adding the necessary amounts of pure components in the master slag.

Experimental Procedure

The experimental method consisted of submerging of the chromite cylinders in a liquid melt of appropriate composition held in a graphite crucible. To provide enough volume for the total immersion of chromite cylinders 120 grams of slag was charged into the graphite crucibles. After the graphite crucible containing the charge is placed in the air tight reaction chamber, argon flushing was started. During the heating up process, the chromite cylinder connected to an alumina tube (8 mm OD, 5 mm ID) by alumina cement was kept about 5 cm above the slag surface. After the initial sample was withdrawn from the slag when the desired temperature was reached, the chromite cylinder was slowly pushed down and immersed in the liquid slag. Samples were withdrawn from the liquid slag at 5, 10, 15, 30, 45, 60, 75, 90 and 120 minutes intervals after the immersion. The samples acquired from the melt by using stainless steel rods (6-8 mm in diameter) was quenched in water. The samples, after weighed and ground in an agate was sent to Mintek Analytical Division for SiO_2, Al_2O_3, MgO, CaO, total-Fe, and total-Cr analysis.

RESULTS AND DISCUSSION

The dissolution was measured in terms of the per cent total chromium passing from the chromite cylinder into the slag and represented as "Passed, Cr, %". Because the total mass of the samples removed from the system for analysis is significant in relation to the initial mass, and the deviation in the cylinder masses can account to 10-15% per cent of the cylinder weight they must be included in the calculations. Thus, "Passed Cr, %" was calculated by

$$PassedCr,\% = \frac{Cr_{slag}(g)_{t=t} - Cr_{slag}(g)_{t=0} + \sum Cr_{samples}(g)_t}{Cr_{cylinder}(g)_{t=0}} \quad (1)$$

Where $Cr_{slag}(g)_{t=t,0}$ is the mass of the total elemental chromium (g) in the slag at time=t(min) and time=0, $\sum Cr_{Samples}(g)_t$ is the cumulative mass of the total elemental chromium (g) taken out of the system in the slag samples excluding the one at time t(min), and $Cr_{Cylinder}(g)_{t=0}$ is the mass of the total elemental chromium(g) in the starting cylinder.

The effect of slag composition on the dissolution of chromite was investigated at 1535°C with stationary cylinders. The slags with compositions given in Table II were contained in graphite crucibles to create reducing conditions. The "Passed Cr, %" values obtained by employing the results of the chemical analysis of the samples, acquired during the experiments, into Equation 1 are given in Table III.

Table III: The Passed Cr(%) values obtained from the experimental points given in Table III. Conducted by use of graphite crucibles at 1535°C with stationary cylinders.

	Experimental			Design point designation					
t,min	i	ii	iii	iv	v	vi	vii	viii	ix	x
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	4.58	1.00	18.66	39.01	4.97	85.89	71.53	0.90	11.90	5.51
10	8.34	2.00	43.19	43.05	5.10	99.99	73.53	1.50	13.76	6.72
15	8.98	3.80	42.05	38.58	5.44	40.55	68.34	2.60	13.09	6.95
30	10.20	5.60	38.27	41.76	9.78	39.22	37.35	3.50	16.52	8.89
45	11.54	6.10	30.40	37.27	13.12	27.04	32.67	4.80	15.70	8.48
60	13.03	6.80	24.20	43.55	17.62	19.84	32.89	5.12	15.50	10.28
75	12.33	7.20	21.98	43.36	17.10	25.20	33.10	6.21	15.69	10.28
90	15.24	8.04	21.59	47.81	19.16	27.53	32.90	7.25	15.33	10.28
120	15.22	8.08	21.65	46.65	18.95	25.86	33.10	7.21	15.45	10.28

	Experimental			Design point destination					
t, min	xi	xii	xiii	xiv	xv	xvi	xvii	xviii	xix	xx
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	65.43	0.00	0.50	0.00	57.95	12.22	81.15	0.70	14.73	16.53
10	58.27	0.00	1.60	0.00	43.28	14.22	94.48	1.60	22.80	17.73
15	35.09	0.00	2.20	0.00	39.57	19.67	53.45	2.40	27.80	19.83
30	22.82	0.00	3.80	0.00	36.44	11.45	45.22	3.20	35.24	15.28
45	32.17	0.00	4.43	0.00	34.72	16.86	36.52	4.60	24.61	13.50
60	34.48	0.00	5.43	0.00	37.59	21.27	39.70	5.49	25.03	14.35
75	38.21	0.00	6.77	0.00	37.20	27.26	34.50	5.69	23.83	14.98
90	35.98	0.00	8.98	0.00	38.32	23.92	31.29	5.69	23.45	14.38
120	36.34	0.00	9.01	0.00	37.20	26.65	33.70	5.69	23.12	14.45

The results at each particular period were employed into a quadratic equation (Equation 2) to describe the response surface encountered in the previously given experimental region at a given period (eg. 5, 10, 15, 30, 45, 60, 75, 90 and 120 minutes). The quadratic equation is given as:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + + b_{24}x_2x_4$$

$$.. + b_{24}x_2x_4 + b_{34}x_3x_4 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{44}x_4^4 \qquad (2)$$

Where, y = response, b_0 = intercept, x_1 = %SiO_2, x_s = %Al_2O_3, x_3 = %MgO, x_4 = %CaO.

Although it is obvious that the effect of slag composition on the chromite dissolution should be investigated with the other variables constant the melting points of the compositions II, III, VI and XVI are above 1535°C; these four experiments were conducted at their melting points and it was expected that this would cause a discrepancy between the theoretical and the experimental results. However, it was observed that there was a good agreements between the two. Figures 2 and 3 are given as an example to this, in almost all of the experimental points given in Table III a similar match and trend was observed. These figures show the curves obtained by the application of real and the calculated values of percent chromium passing from the chromite cylinder into the melt as a function of time at the given temperature and slag composition.

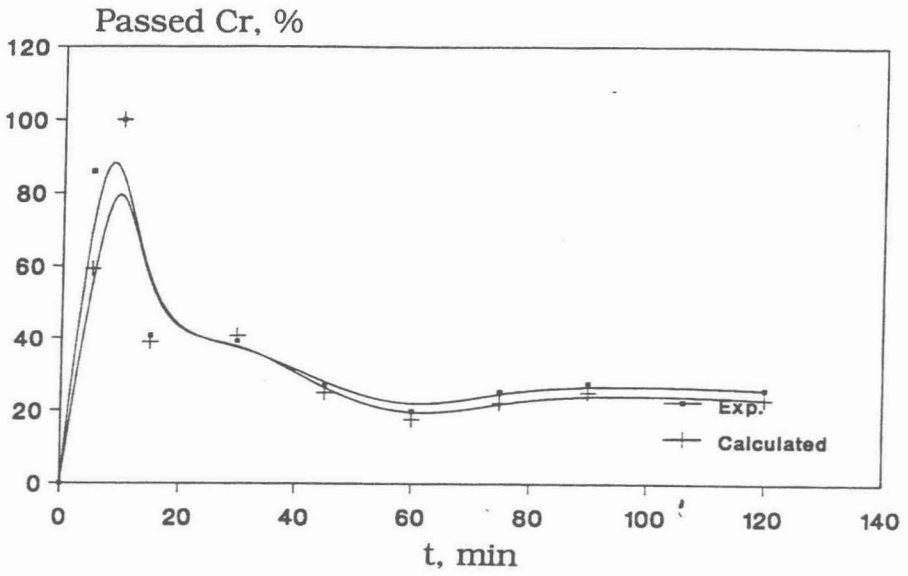

Fig. 2. A comparison between the experimental and calculated data. Dissolution of chromite as a function of time in slag type VI (Table II) at 1690°C with stationary cylinders.

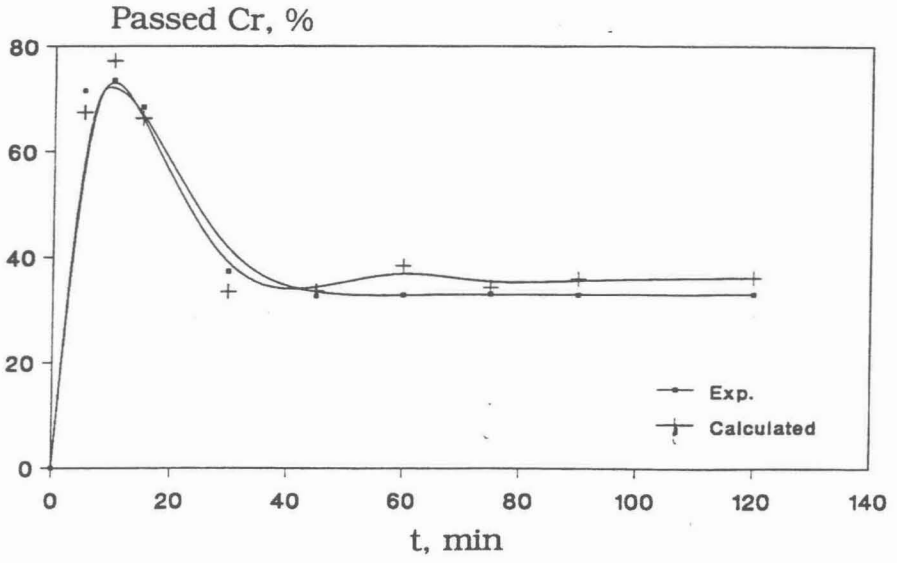

Fig. 3. A comparison between the experimental and calculated data. Dissolution of chromite as a function of time in slag type VII (Table II) at 1535°C with stationary cylinders.

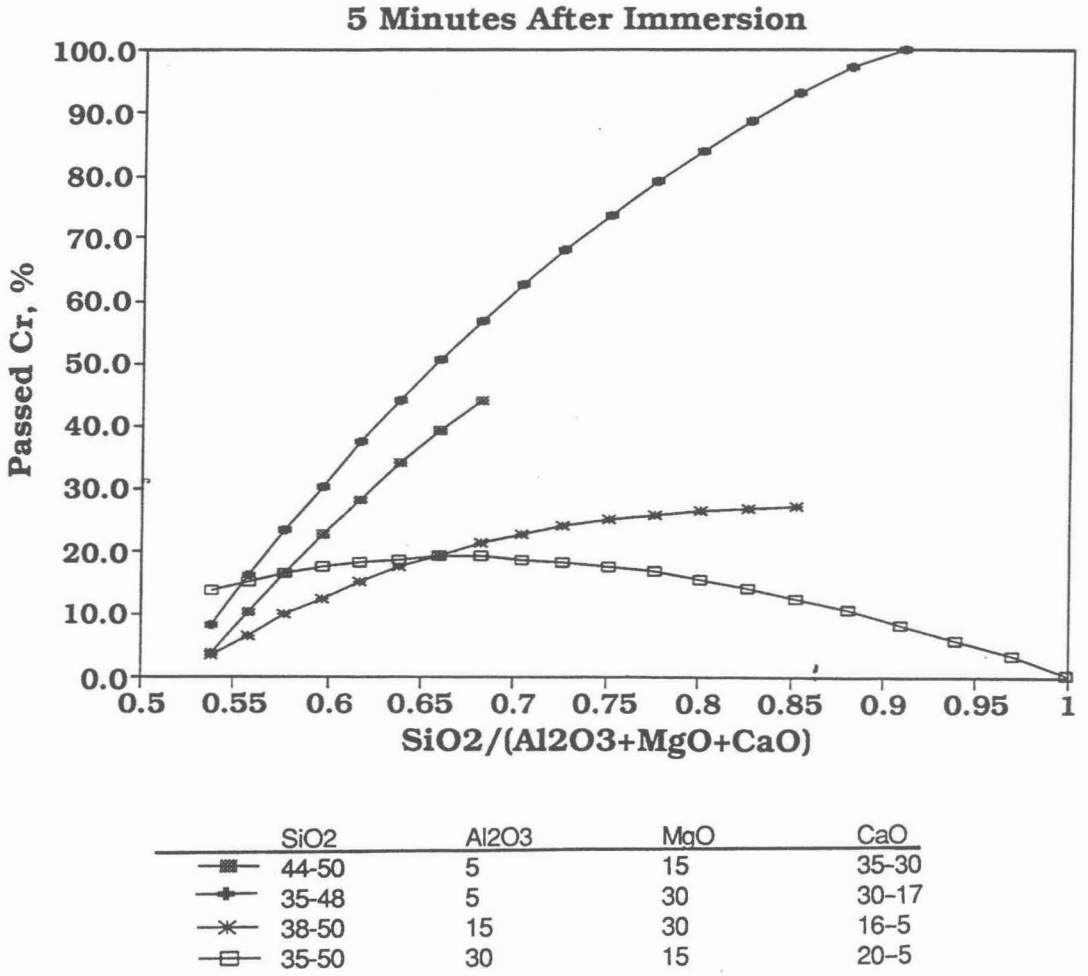

Fig. 4. The effect of slag activity on the chromite dissolution at 1535°C with no rotation, at the end of 5 minutes. Plots were constructed by using the theoretical values.

In all the experimental results, the general trend is that at the initial stages upto 15 minutes reaction time the maximum amount of dissolution takes place. After this stage, the total chromium content of the melt drops to a certain level indicating chromium removal from the liquid slag. This can only occur by the reduction of chromium oxide at the graphite crucible walls. In almost all the crucibles after an experiment there were small nodules of metallics sticking on the walls and even sometimes on the surface of the solidified slag phase. The size of these particles are in the range of tenth of a millimetre to several millimeters, and can weigh upto 2.74 grams, which is about 50 per cent of the metallics in the chromite cylinder. The SEM studies on these particles proved that these particles are consisted of mainly iron and chromium which form the reducible oxides in the chromite cylinder. This indicates that the dissolution of chromite in the liquid slag contained in a graphite crucible takes place parallel with a continuous reduction process on the graphite wall. Urquhart [8] also concluded in his study on the high carbon ferro-chromium production in the submerged arc furnace with

the real size samples that in the presence of slag at temperatures higher than 1540°C the reduction of chromite ore by carbon was very rapid. After the dissolution is completed the chromium oxide and the iron oxide activities in the slag phase reaches their maximum causing the reduction reactions to take place removing the chromium and iron from the liquid slag phase. It seems that when the graphite crucibles are used, the faster the chromite dissolution occurs the faster the removal of iron and chromium from the liquid slag phase takes place by the reduction reactions.

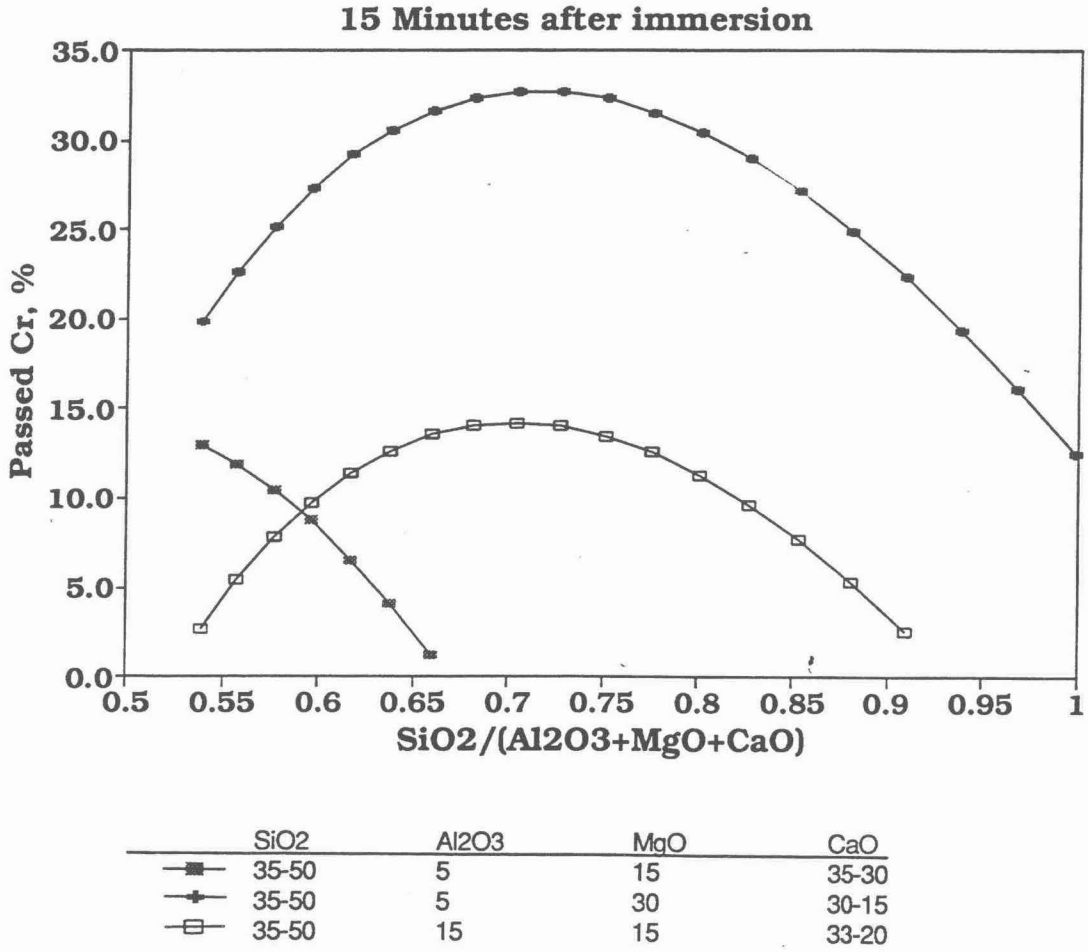

Fig. 5. The effect of slag acidity on the chromite dissolution at 1535°C with no rotation, at the end of 15 minutes. Plots were constructed by using the theoretical values.

Figures 4 to 7 are given as further examples for the effect of reducing conditions on the chromite dissolution. Figures 4 and 5 which were constructed by the theoretical values, show the effect of acidity (i.e. SiO_2/Al_2O_3 + MgO + CaO) on the chromite dissolution in different types of slags at 5 and 15 minutes respectively. The overall dissolution characteristics affected by the "acidity" changes at different at periods. The highest dissolution was achieved with the

slag SiO_2 = 48%, Al_2O_3 = 5%, MgO = 30%, CaO = 17% at 5 minutes (Series 2 in Figure 3). The dissolution was increasing with SiO_2 content increasing from 35 to 48 per cent and CaO content decreasing from 30 to 17 per cent at constant Al_2O_3(=5%) and MgO(=30%) contents. At 15 minutes (Figure 4) the highest dissolution was also indicated by the same type of slags but this time reaching a maximum at about 30 per cent instead of 100 per cent which was obtained at 5 minutes.

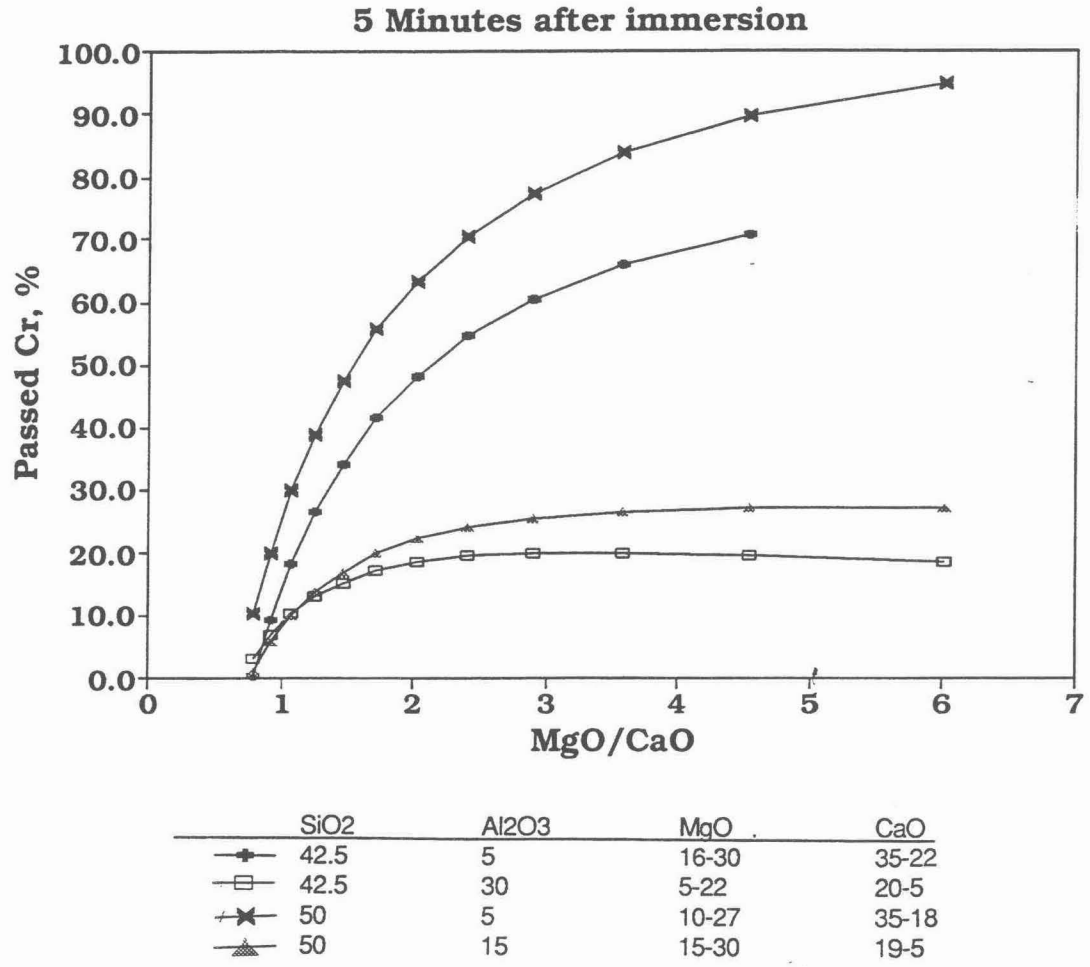

Fig. 6. The effect of MgO/CaO ratio of the slag on the chromite dissolution at 1535°C with no rotation, at the end of 5 minutes. Plots were constructed by using the theoretical values.

Figures 6 and 7 were also constructed by the calculated values. They show the effect of MgO to CaO ratio on the chromite dissolution obtained with different types of slags with constant SiO_2 and Al_2O_3 contents at 5 and 15 minutes respectively. At 5 minutes the dissolution increases with the increasing MgO/CaO ratio. And at 15 minutes the increasing MgO/CaO

ratio has an adverse effect on the dissolution upto a certain limit. After a minimum this effect is reversed showing an increase in the dissolution with increasing MgO/CaO.

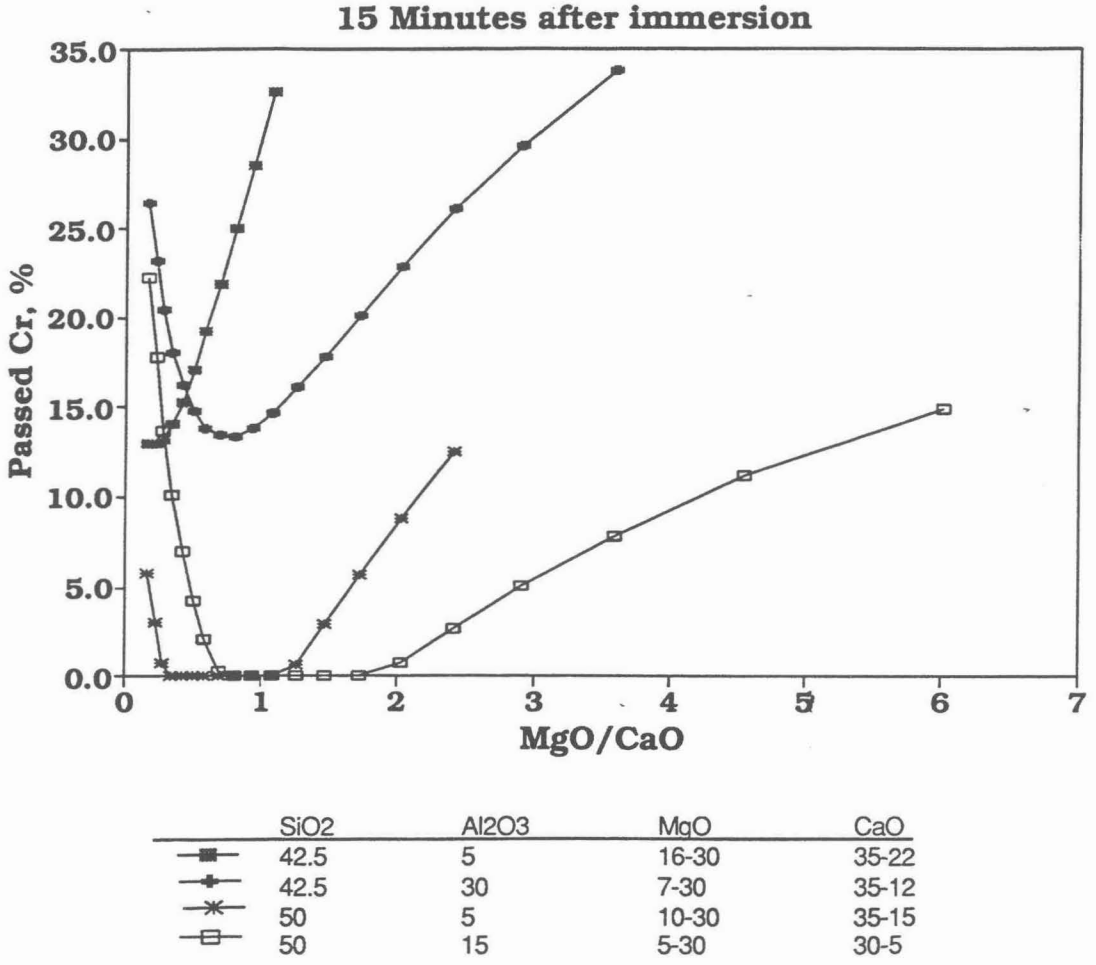

Fig. 7. The effect of MgO/CaO ratio of the slag on the chromite dissolution at 1535°C with no rotation, at the end of 15 minutes. Plots were constructed by using the theoretical values.

The change in the chromite dissolution characteristics wiht time prevents to draw further conclusions. The results obtained from the experiments using graphite crucibles can only be meaningful when the same set of experiments are repeated in neutral conditions for a reference. Also the data obtained has to be studied as a whole for a meaningful statistical analysis.

CONCLUSIONS

The dissolution of chromite in liquid slags contained in graphite crucibles takes place parallel with the reduction of iron oxide and chromium oxide at the crucible walls. The complete dissolution takes place comparatively fast. When the chromite cylinder dissolves the chromium and iron content of the slag together with the other constituents which form the chromite phase increase to a maximum, then a certain amount of iron and chromium removal occurs via the reduction of $FeO.Cr_2O_4$ by the carbon supplied by the graphite crucible. The reduction of the oxide phase takes place at the crucible walls indicating the transport of oxide phase through the liquid slag phase to the reaction site. The experimental work by using molybdenum crucibles to create neutral conditions together with the SEM-EDS studies on the reacted samples continues.

ACKNOWLEDGEMENTS

The authors thank Mintek and the Ferro Alloys Producers' Association of South Africa for co-sponsoring this work. This paper is published by permission of Mintek.

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