

THE DISSOLUTION OF A TRANSVAAL CHROMITE
IN LIQUID SILICATE SLAGS UNDER NEUTRAL
CONDITIONS BETWEEN 1545 AND 1660°C

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SYNOPSIS

The compositions of silicate slags, with CaO/SiO₂ mass ratios between 0.03 and 0.55 in equilibrium with a gangue-free Transvaal chromite were determined. The slags were equilibrated with porous chromite crucibles under an argon atmosphere in a vertical-tube resistance-heated furnace. The maximum solubilities of the constituents of chromite spinel (MgO, Al₂O₃, and Cr₂O₃) under these conditions were determined. The solubility of Cr₂O₃ solubility was always less than 1.5 per cent (by mass), and the solubilities of MgO and Al₂O₃ were substantially less than the MgO and Al₂O₃ contents of the slags used industrially for chromite smelting. These two factors indicate that the dissolution of chromite into slags that are tapped from industrial furnaces is likely to be slow. This may in turn be the reason for the observed appearance of undissolved chromite in the discard slags from large submerged-arc furnaces in which chromite is smelted.

Note: all chemical compositions in this paper are expressed in percentages by mass.

INTRODUCTION

Chromite, the ultimate source of all the chromium in stainless steels, is currently smelted in submerged-arc electric furnaces to produce high-carbon ferrochromium for subsequent addition to the steelmaking process. The chromium content of the discard slags from these furnaces effectively determines the chromium recovery, and is therefore an important process variable.

Oosthuyzen and Viljoen⁽¹⁾ recently carried out a mineralogical investigation

of the slags from three different plants in South Africa. They found that, at those plants which experienced high losses of chromium (i.e. more than 11 per cent chromium in the slag), more than 60 per cent of this chromium was contained in 'undissolved and partly altered chromite particles'. The presence of these chromite particles in the slags implies that the dissolution of chromite plays an important role in its smelting. Kouroki et al⁽²⁾ have suggested that the dissolution of $MgCr_2O_4$ into molten slags is likely to be the rate-limiting step in the plasma smelting of mixtures of chromite and iron ore. Fujita et al⁽³⁾, using a 550 kg converter, found that slags containing more than 45 per cent MgO plus Al_2O_3 at $1600^\circ C$ have slower reduction rates, and attribute this to the formation of a layer of MgO - and Al_2O_3 -rich spinel around the chromite particles. This layer disrupts the dissolution of the chromite. However, Fukagawa and Shimoda⁽⁴⁾ concluded that the dissolution of particles of chromium ore into the molten slag was not the rate-limiting step under static conditions.

The dissolution of chromite is therefore of interest not only for the current submerged-arc process, but also for the new plasma-smelting process⁽⁵⁾, and for possible development of a process based on energy from combustion using a combined blown converter⁽³⁾. The solubility of chromite in a silicate slag was therefore investigated in order to acquire the basic equilibrium data, a longer-term objective being a study of the kinetics of the dissolution process itself.

EXPERIMENTAL METHOD.

A 200 kg sample of chromite from the LG-6 layer of the Bushveld Complex⁽⁶⁾ was obtained, and 75 kg of concentrate with a SiO_2 plus CaO content of less than 0.2 per cent was produced by grinding and tabling to remove the gangue (Table 1).

Chromite crucibles (55 mm high and 36 mm in diameter) were made from this material by hand-ramming, drying, and sintering under an argon atmosphere at $1550^\circ C$ for 1 to 2 hours. An aqueous solution of chromium trioxide was used as a binder for the hand-ramming operation. No significant difference was found between the composition of the chromite in the

starting material and in the final sintered crucibles (Table 1). The crucibles had a bulk density of 2.76 g cm^{-3} , a porosity of 38.1 per cent, and a typical mass of 92 g.

A range of synthetic slags was prepared from commercial grades of limestone, quartz, magnesia, and alumina by melting in a small graphite-lined arc-furnace. The molten slags were cooled, ground, and roasted at 550°C for 16 hours to oxidize any graphite or metallic iron present. The compositions of the seven slags are shown in Table 2.

A vertical alumina-tube furnace with a molybdenum-wire heating element was used to maintain the sample at a constant temperature ($\pm 5^\circ\text{C}$) under an atmosphere of spectrographic-grade argon (total impurities less than 0.002 per cent by volume). The chromite crucibles were filled with approximately 20 g of one of the synthetic slags, and then raised under sealed conditions into the hot zone of the furnace over a period of 45 minutes. The samples were usually held in the hot zone for 1 hour but were occasionally held for up to 12 hours. They were then lowered rapidly (within 30 seconds) into a cold zone (less than 200°C) of the furnace under argon for cooling and final removal. The temperature, which was measured throughout the run, varied by an average of 6°C , while the standard deviation of the change in sample mass after the runs was 0.15 g.

The crucibles and the contained slag (most of which had penetrated the porous crucible walls) were sectioned and examined mineralogically. Phases within the crucible walls were analysed by energy-dispersive spectroscopy (EDS) or by use of an electron microprobe.

RESULTS

The slag that had penetrated the porous walls of the chromite crucibles was observed to have interacted with the chromite grains close to the inner surface of the wall in a variety of ways (Figure 1) depending on the composition of the slag charge. The interaction was usually confined to the edges of the chromite grains, and took the following forms:

- (a) entire portions of the original

outer surface of the spinel were removed, leaving a chromite grain of drastically altered appearance (slag no.7),

- (b) the original surface of the spinel was unchanged, but the centre and edges of the crystals became visibly zoned (slag no.3),
- (c) crystals of secondary spinel precipitated on the edges of the chromite grains (slag no.4), or
- (d) no visible interaction occurred (slag no.6).

The alteration of the surfaces of the chromite grains decreased with increasing distance from the inner surface of the crucible wall regardless of the form of the alteration.

The compositions of the edges of the chromite grains in contact with a slag phase at inner, middle, and outer positions of the crucible wall showed a convergence towards the original composition in all cases (Figure 2). The centres and edges of chromite grains in the outer portion of the crucible were analysed and compared to detect any concentration gradient within the grains. The differences in the analyses were typically less than one standard deviation. These analyses (centre and edge) were then averaged and compared with the chemical analyses of the original chromite and the average EDS analysis of four chromite grains (centre and edge) in a blank crucible (i.e. one that had undergone the same experimental procedure without a slag charge). The differences between the analyses were found to be within the limits of experimental error for the various methods of determination (Table 1.)

The absence of an experimentally significant concentration gradient in chromite grains in the outer region of the crucible wall, even in the samples that had been held in the hot zone of the furnace for up to 12 hours, led to the conclusion that the slag and chromite at these positions were in chemical equilibrium, and that the slag in contact with the chromite was therefore saturated with respect to constituents the chrome spinel.

The determination of the equilibrium slag

was complicated in many cases by the formation of a secondary crystalline phase upon cooling. The relative proportions of the crystalline and matrix phases present in these cases were estimated visually, and were checked by an EDS image-analysis technique, which indicated that a likely error of ± 10 per cent could be expected. The effect of this error, including the assumption that the density difference was negligible, was frequently reduced because of the similar compositions of the crystalline and matrix phases. A further estimate of the likely error in this procedure was made from a comparison of the CaO/SiO₂ ratio determined in this way with the initial CaO/SiO₂ ratio in the slag (Figure 3).

The estimated equilibrium compositions of the slag are shown in Figures 4 and 5. The data denoted (FeO)_T were calculated from the total iron detected expressed stoichiometrically as FeO, although clearly a significant proportion of Fe₂O₃ should be present. The estimated errors in these compositions were less than 2.0 per cent for MgO, Al₂O₃, and (FeO)_T, and less than 0.1 per cent for the Cr₂O₃.

DISCUSSION

The mechanism by which the slag approaches equilibrium with the chromite is presumed to be the repeated transfer of mass between the slag and the edges of the chromite grains as the slag flows outwards through the porous wall of the chromite crucible. Since the phases were analysed by EDS or with the electron microscope, the oxidation state of the iron could not be determined. The usefulness of the technique is therefore limited, although it does provide a useful starting-point for the detailed study of complex systems in which the number of components makes the use of a classical bracketing technique extremely laborious.

The increase in the solubility of MgO, Cr₂O₃, and (FeO)_T with increasing temperature was in accord with expectations. However, the solubility of Al₂O₃ in slags with CaO/SiO₂ ratios of less than 0.3 decreased from 1550°C to 1650°C (Figures 4 and 5). The reason for this behaviour is not known, and further experiments with controlled Fe²⁺/Fe³⁺ ratios in the slag may be necessary.

The very low solubility of Cr_2O_3 (less than 1.5 per cent) in the slag therefore limits the solubility of the chromite particles. Under conditions of practical smelting, chromite would dissolve only in conditions that were sufficiently reducing to maintain the Cr_2O_3 content of the slag well below this value. The presence of pure solid carbon at 1650°C will satisfy this condition thermodynamically, but the transport of the Cr_2O_3 dissolved in the slag, either by diffusion or by convection, will be constrained by the low solubility of Cr_2O_3 , which limits the concentration gradient or driving force. The static slag/chromite conditions in Fukgawa and Shimoda's experiments⁽⁴⁾, and the fact that an increase in the MgO and Al_2O_3 contents of the slag-reduced the reduction rate, point towards the rate of diffusion of Cr_2O_3 in the slag as the rate-limiting step in this case.

The solubilities of MgO and Al_2O_3 at 1650°C that were determined in the present study (6.0 and 16.0 per cent respectively) are significantly lower than the MgO and Al_2O_3 contents of the industrial slags (with similar CaO/SiO_2 ratios) investigated by Oosthuyzen and Viljoen⁽¹⁾ (20.0 and 25.0 per cent respectively). It would therefore be expected that chromite entering a similar slag would not dissolve immediately even if the conditions were sufficiently reducing and the slag were sufficiently well stirred to overcome the constraints on the transport of dissolved Cr_2O_3 . These constraints were demonstrated experimentally by Fujita *et al*⁽³⁾ in a well stirred smelting-reduction converter.

CONCLUSIONS

The compositions of silicate slags in equilibrium with gangue-free Transvaal chromite as a function of CaO/SiO_2 at 1550°C and 1650°C have been determined using a porous chromite crucible technique. The low solubility of Cr_2O_3 in these slags (< 1.5 per cent) implies that strongly reducing and well stirred slag conditions would be required to ensure the rapid dissolution of chromite. Another limitation to chromite dissolution would be expected if the MgO and Al_2O_3 contents of the slag were more than 6.0 and 16.0 per cent respectively at 1650°C and at a CaO/SiO_2 ratio of 0.3.

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CAPTIONS FOR ILLUSTRATIONS

- FIGURE 1. Interaction of slag with chromite grains at the inner surface of the wall of the chromite crucible.
- FIGURE 2. Compositional changes in the edges of chromite grains with increasing distance from the inner wall of the crucible.
- FIGURE 3. Comparison of the CaO/SiO_2 mass ratios in the synthetic slags with those measured in the slag in the outer portions of the crucible wall
- FIGURE 4. Compositions of slags in equilibrium with chromite between 1545 and 1560°C
- FIGURE 5. Compositions of slags in equilibrium with chromite between 1645 and 1660°C

Table 1
 Comparisons of chromite compositions
 (expressed in percentages by mass)

Sample	ANALYTICAL METHOD NUMBER OF SAMPLES STATISTIC	Head sample		Blank run		Chromite grains in contact with slag	
		XFS	Mean	XFS	Mean	EDS	Mean
Cr ₂ O ₃		47.5		47.9		48.5	
FeO		18.5		18.2		ND	1.2
(FeO) _T		25.3		25.0		26.2	ND
MgO		9.8		9.8		11.3	1.3
Al ₂ O ₃		13.1		12.9		13.0	0.7
SiO ₂		<0.3		<0.3		<0.1	1.2
CaO		<0.2		<0.2		<0.1	ND
TiO ₂		0.6		0.5		0.2	ND
						48.3	0.1
						ND	σ
						25.1	
						11.0	
						14.4	
						<0.1	
						<0.1	
						0.3	

Size analysis : 27% 150 μm, 16% 75 μm, 0.4% 38 μm

XFS X-ray-fluorescence spectroscopy
 EDS Energy dispersive spectroscopy
 σ Standard deviation
 ND Not determined
 FeO Was analyzed by wet chemistry
 (FeO)_T Total iron expressed as FeO

Table 2
 Compositions of the synthetic slags
 (expressed in percentages by mass)

Constituent	Slag no.						
	1	2	3	4	5	6	7
SiO ₂	53.5	52.0	52.7	42.2	44.3	55.1	55.0
CaO	25.6	20.6	2.0	11.4	1.1	4.0	35.9
MgO	13.0	9.8	18.2	26.0	23.1	29.4	4.5
Al ₂ O ₃	4.0	14.4	24.3	18.0	28.8	8.9	1.4
Cr ₂ O ₃	0.02	0.02	0.10	0.22	0.02	0.02	0.09
FeO	0.5	1.0	0.3	0.3	0.8	0.5	0.8
Fe ₂ O ₃	0.1	0.1	0.2	0.1	<0.1	0.1	0.1
Na ₂ O	0.03	0.02	0.16	0.12	0.09	0.04	0.05
K ₂ O	0.05	0.04	0.02	0.04	0.05	0.07	0.04
CaO/SiO ₂	0.48	0.40	0.04	0.27	0.03	0.07	0.65

Notes

- (1) For all slags: MnO < 0.15 %
 : TiO₂ < 0.20 %
 : ZnO < 0.003 %

(2) Fe₂O₃ = (total iron) - (FeO)

(3) Analyses by X-ray fluorescence spectrometry except
 Cr₂O₃ and FeO : wet chemical
 Na₂O, K₂O, and ZnO : atomic absorption spectrometry



Slag no. 4



Slag no. 7



Slag no. 6



Slag no. 3

FIGURE 1. Interaction of slag with chromite grains at the inner surface of the wall of the chromite crucible

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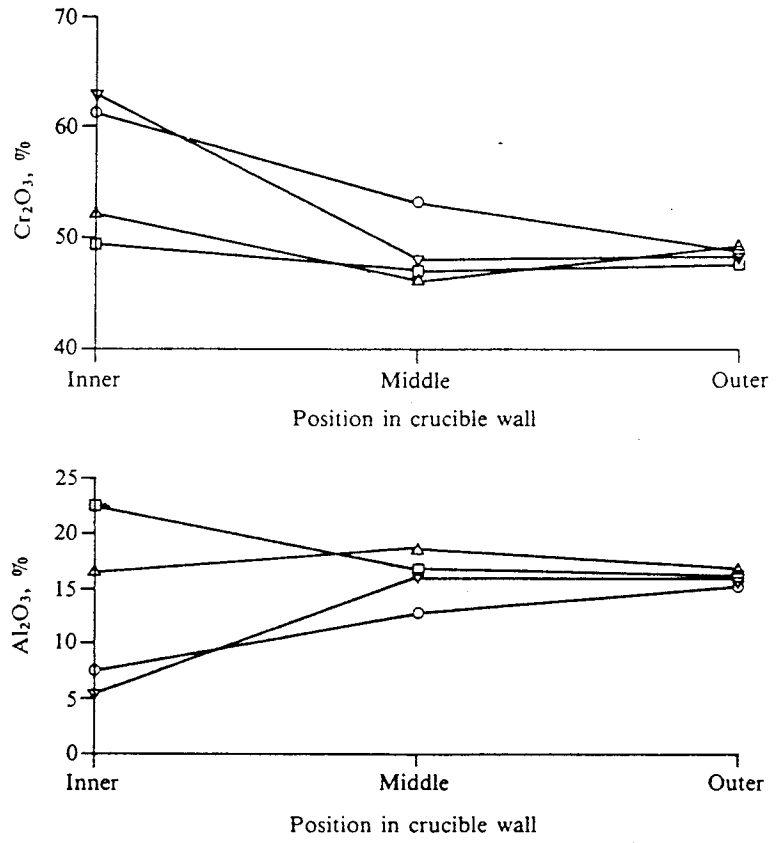


FIGURE 2. Compositional changes in the edges of chromite grains with increasing distance from the inner wall of the crucible

~~72~~ Purity - 72%

990p

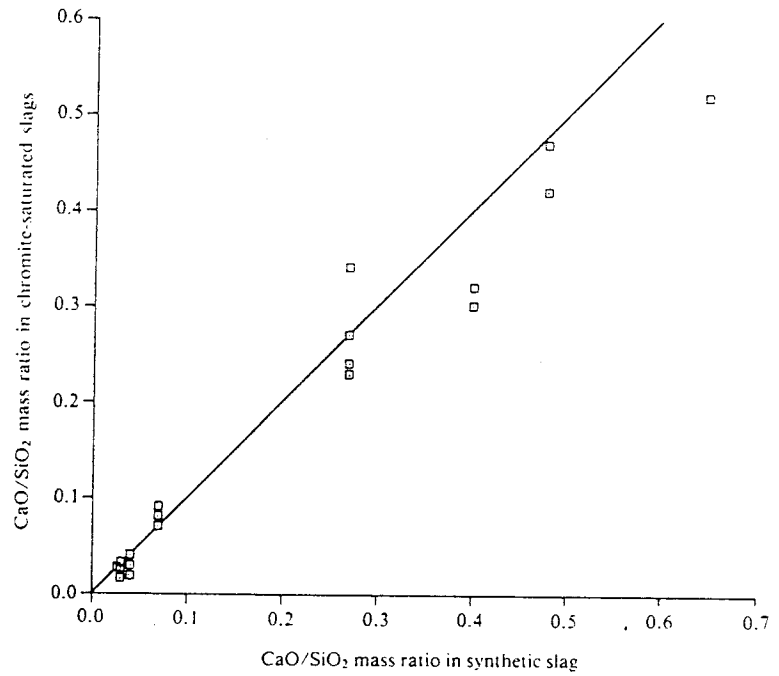


FIGURE 3. Comparison of the CaO/SiO₂ mass ratios in the synthetic slags with those measured in the slag in the outer portions of the crucible wall

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