ASPECTS OF SAF SMELTING OF FERROCHROME

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ABSTRACT

This paper provides a review of the chemical reactions occurring in the submerged arc processing of chromite ores. The excavations of industrial furnaces have shown that the charge, as it descends through the furnace, passes through a number of distinct reaction zones. Each zone is characterised by differing process conditions and reaction products. The phase equilibria, reaction steps and mechanisms occurring as the charge progresses through the furnace are examined, and the potential influences of these factors on the process outcomes are discussed.

1. INTRODUCTION

This review of mechanisms and kinetics of chromite reduction presented is focused on providing insight into the reactions occurring during ferrochrome smelting by submerged arc furnace technologies. The approach taken in the review is to specifically follow and examine the reaction steps that result in the formation of metal.

From investigations of excavated quenched submerged arc furnaces, and previous overviews of the technology and the process steps [1-8] the following idealised reaction zones have been identified (see Fig. 1). *Note however that the exact positions of these zones appear to vary with furnace design and operating practice. The zones do not necessarily follow a simple layered structure as was envisaged in early models of the process.*
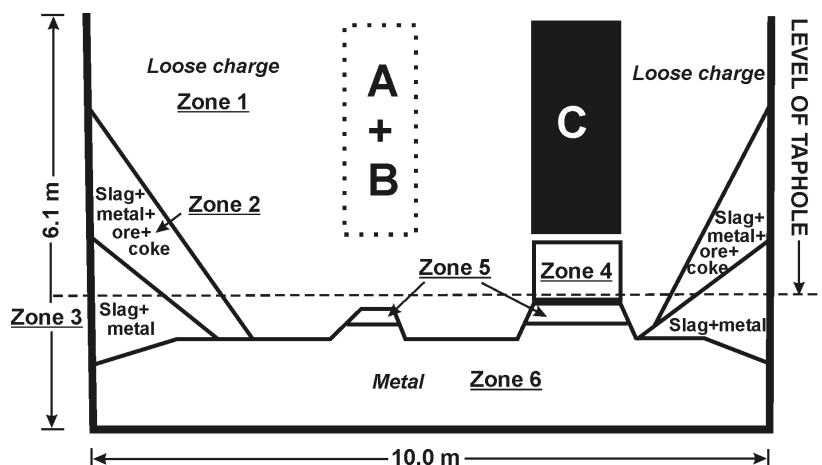

Figure 1. Schematic diagram of the reaction zones in submerged arc furnace for ferrochromium production (principally [8])

1.1 Upper furnace Zone 1 Loose charge

The loose charge zone extends from the charge layer down to near to the tip of the electrode.

The following reactions occur in this zone;
- Preheating of the charge.
- Decomposition of limestone fluxes e.g. $CaCO_3$, and other minerals.
- Gasification of carbon; reaction with air and CO_2.
- Gaseous reduction of chromite ore and partial metallisation of iron and chromium oxides.

According to Ringdalen [8] "most of the volume in the submerged arc furnace is loosely sintered burden". The average retention time in this zone was estimated to be 24 hours, but only approximately 20% of reduction of the charge takes place in this loose charge zone; no liquid slag is formed.

Yamagishi [2] demonstrated, through the use of alumina tracers, that the burden material descended in a V-shaped distribution, and rate of descent reaches a maximum at positions between the furnace walls and the electrodes and between the electrodes themselves.

Temperature profiles and excess gas pressures in this zone were measured by Ostrovskii [4] and quoted by Kossyrev and Olsen [7]. These data show that the 1600°C isotherm was achieved only close to the electrode tips, and that above 1673K the gas pressure rises rapidly, the later temperature corresponding to the onset of slag formation.

1.2 Lower furnace (Zones 2-6)

1.2.1 The reactions occurring in the lower furnace involve;
Slag formation
Dissolution of chromite in slag
Reduction of metal from the slag phase and metal alloy formation
Alloy/slag separation

1.2.2 Sidewall slag/metal/ore/coke (Zone 2)
Banks of rigid, partially fused/partly-reduced material are formed in zone 2 adjacent to the furnace walls. These banks are thickest at distances furthest from the electrodes.

1.2.3 Sidewall/Slag/metal (Zone 3)
The material below zone 2 contains mixtures of slag and metal.

1.2.4 Beneath the electrodes (Zone 4)
There is some uncertainty in the literature about the material present immediately under the electrode tips. These zones do not connect with the similar zones under the other electrodes (A, B, C). Yamagishi [2] indicates the presence of a void may have been due to contraction of the bed during cooling of the furnace; Wedepohl and Barcza [5] report slag and coke under two electrodes but mainly slag under the third electrode; Ringdalen [8] indicates the presence of a coke bed, containing a mixture of melted gangue minerals, fluxes and MgO and Al_2O_3 liberated from the chromite during reduction. Due to the formation of partially solidified charge materials around the electrodes (zones 2 and 3) the active slag reduction zone is restricted in size. The residence time in the high temperature smelting zone, defined here as the coke bed (zone 4), is relatively short, possibly of the order of 30-40min.

1.2.5 Slag (Zone 5)
Yamagishi [2] and Wedepohl and Barcza [5] found a distinctive slag layer; Ringdalen [8] however, report that "no distinctive slag layer was found". Yamagishi [2] and Kossyrev and Olsen [7] both report the presence of a large region of "unmolten partly reacted lumpy ore" between the slag and metal.

1.2.6 Metal (Zone 6)
All previous studies show the formation of a distinct liquid metal alloy layer at the base of the furnace.

2. REACTION STEPS

The chromite charge to the furnace is principally in the form of lump ore and /or pellets. The lump ore material consists of chromite grains surrounded by solidified host rock (Fig. 2). Pellets are made from chromite concentrates that have been agglomerated and pre-treated to form spherical particles (Fig. 3). The grain size and microstructures of the chromites are variable from dense rounded grains in the lump to highly fractured acicular grains in the pellets. The particle size ranges of lump, pellet and coke are controlled to maximise bed permeability. Chromite grains are not necessarily uniform in composition since there are variations between ore bodies, and even between and within ore seams. The chromite forms part of the spinel crystal family, having the general formula $(Fe^{2+}, Mg^{2+})O.(Al^{3+}, Cr^{3+}, Fe^{3+})_2O_3$.

As the charge descends and passes through the reaction zones various reactions occur during metal alloy formation. These reaction steps are now reviewed in more detail.
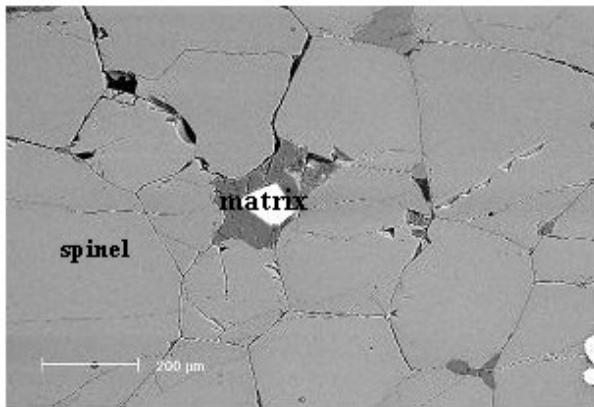

Figure 2. Micrograph illustrating the typical structure of South African lump chromite ore.
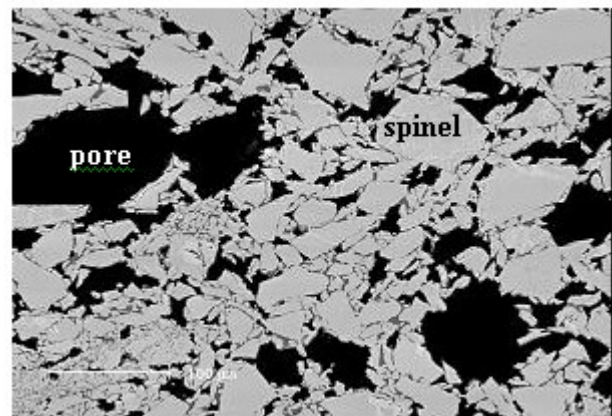

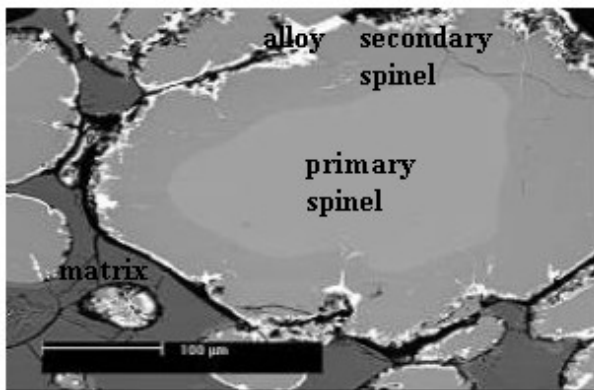Figure 3. Micrograph illustrating the structure of a chromite pellet.

Figure 4. Micrograph of South African lump chromite reduced 1473K, 4 h, CO gas.
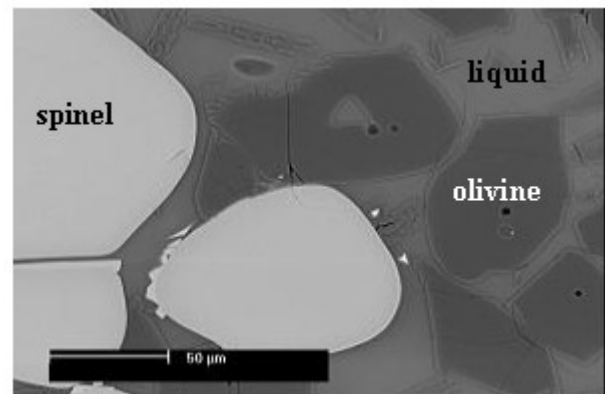

Figure 5. Micrograph of South African lump chromite reduced 1673K, 0.5 h, CO gas.

2.1 Gaseous reduction of chromite

The mechanisms and kinetics of gaseous reduction of solid South African chromites ore have been studied by a number of workers [9-29]. There appears to be general agreement that in the loose charge (zone 1) iron is preferentially reduced from the solid chromite grains by reaction with carbon monoxide gas produced in the lower furnace.

The rate limiting reaction mechanism during the gaseous reduction of dense chromite grains is the ionic diffusion of metal species in the solid spinel phase. Soykan et al [19] proposed that the reduction of chromite occurs by the following sequence of reactions;

a) "Initially, Fe^{3+} and Fe^{2+} at the surface of the chromite particle are reduced to the metallic state. This is followed immediately by the reduction of Cr^{3+} ions to the divalent state.

b) Cr^{2+} ions diffusing toward the centre of the particle reduce the Fe^{3+} ions in the spinel under the surface of the particle to Fe^{2+} at the interface between the inner and outer cores. Fe^{2+} ions diffuse towards the surface, where they are reduced to metallic iron.

c) After the iron has been completely reduced, Cr^{3+} and any Cr^{2+} that is present are reduced to the metallic state, leaving an iron- and chromium- free spinel, $MgAl_2O_4$".

The partially altered chromite contains a dispersion of fine iron/chromium metal alloy particles. The solid alloy, formed in the early stage of reduction as the charge descends and is heated through zone 1, is low in chromium. As the reaction time and temperature increases, the chromium concentration in the alloy increases. In later stages of reduction chromium - iron carbides are observed to form [17,19].

The thermodynamics of reduction behaviour of iron-chromium ore in the presence of carbon are discussed by Hino et al [24]. These authors predict the stable phase assemblages as function of temperature and CO/CO_2 gas mixtures for Fe-Mg-Cr and Fe-Mg-Cr-Al spinels in the absence of fluxes. As reduction proceeds at progressively higher temperatures the sequence of stable phases expected at carbon saturation with South African ores is:

1390K, solid Fe + $(Fe,Mg)O.(Cr,Al)_2O_3$;
1470K, liquid Fe + $(Fe,Mg)O.(Cr,Al)_2O_3$;
1670K, liquid Fe + $(Cr,Fe)_7C_3$ + $MgO.(Cr,Al)_2O_3$;
1850K, liquid Fe + Cr_3C_2 + $MgO.Al_2O_3$.

In general the reaction proceeds topochemically, from the surface of the particle in the case of dense ore or from the surface of individual grains for porous materials. In cross section, this compositional variation within a grain is seen in the form of a core of primary spinel surrounded by continuous shell of secondary spinel of variable composition. The composition and thickness of the shell varies with slag composition, temperature, oxygen potential and reaction time (Fig. 4). The Fe-Cr alloy forms initially on the outer surfaces of the grains or along microcracks.

The rate and extent of reduction of the chromite ore is dependent on the chemical composition of the chromite, grain and particle size, porosity, and temperature history in pre-treatment and in the furnace [23]. Chromite ores are not uniform in composition; they vary widely with source of material particularly in iron concentration. The relationship between the degree of reduction and the chromium reduction therefore depends on the initial composition.

Since the rate limiting reaction mechanism involves solid-state diffusion, diffusion path length is a critical factor determining reaction rate. The ionic flux to the gas/solid interface is inversely proportional to the distance, so that reduction rate is enhanced with decreasing particle and grain size. Even cracks and sub-grain boundaries within the grains enhance the rates of reduction of individual chromite grains. The reduction rates of individual grains in pelletised materials are significantly faster than in lump material because of the smaller grain sizes and the higher porosities of the pellets.

The rate of reduction of the chromite can also be influenced by the composition and proportion of matrix material in the particles, since this material fuses and eventually melts as the charge descends through the furnace. The formation of the liquid phase can have multiple effects. If there is a high proportion of matrix material the porosity of the ore, and consequently the ease of reducing gas penetration into the particle, may be diminished (Fig.5). On the other hand the partially reduced spinel may react with and dissolve in the molten slag phase, decreasing the effective particle size and influencing the temperature at which the grains in the chromite particles become dispersed in the bulk slag.

The preprocessing of the run-of-mine ore to produce concentrates and pellets is clearly targeted at enhancing the reduction characteristics of the ore to ensure maximum reduction takes place through gaseous reduction. The effects of preprocessing on the kinetics of reduction have been reported in a number of studies [24-29].

2.2 Release of iron/chromium alloy, carbide and chromium into slag as a result of the dissolution of spinel

Ringdalen [8] indicates that most of the reduction takes place in the coke bed situated below the electrode tips. In the particular furnace investigated the coke bed was estimated to be 0.8-1.0m high and 1.5m wide (the width of the electrode), and to have an average temperature up to 1973K. Based on the furnace geometry, she estimated that the residence time in this area of the furnace (zone 4) to be 20-30 min. The slag produced following ferrochromium smelting contains significant quantities of chromium in the form of partially altered chromite (PAC) and entrained alloy. According to the results of the Ringdalen [8] study, there is a great variation in the compositions of the chromite and metal particles dispersed in the slag. The variations are attributed to mixing in the loose charge due to high gas flows in zone 1. This variation in degrees of reduction of the chromite entering the reduction zone may equally be explained by the non-uniform movement of the loose charge material as indicated by Yamagishi [2]. Material close to the furnace walls and the electrodes would have longer residence times in zone 1 than material midway between these restrictions. This problem of non-uniform reduction and the risk of insufficient prereduction of chromite would be exacerbated by the restricted cross section formed by the presence of the partially fused material in zone 2 in the furnace. Although the pre-reduction steps result in the reduction of metallic iron from the chromite, the removal of the alloy and the remaining chromium from chromite ore and the slag to form alloy product involves a series of quite different chemical reaction steps and mechanisms.

As indicated in the previous section it has been shown that alloy and carbide are formed during gaseous reduction. It has been shown that a rim of secondary spinel, approaching the composition $MgAl_2O_4$, is formed on the surface of the particles, physically separating the primary chrome-containing phase from the reducing atmosphere and the slag. This secondary spinel must be dissolved in the slag in order to physically release alloy/carbide that has already been formed during pre-reduction and to release the remaining chemically bound iron and chromium in the primary chromite. It has been shown by a number of investigators [30-32,34] that the addition of silica and the resulting formation of liquid slag can dissolve these partially altered chromites (PACs) and enhance the rate of reduction of chromium from the ore. A micrograph showing partially reduced chromite in slag is shown in Figure 6.

The extent to which spinel is dissolved in slag is dependent on:
- Temperature
- Slag composition
- Slag volume
- Oxygen partial pressure
- Residence time in the high temperature zone

The effects of these process variables on spinel dissolution have been investigated in [30-36].

Demir and Eric [33,36] examined the dissolution of sintered chromite ore rods (15mm diam. x 19mm long) in a range of slag compositions at (1873K) under reducing conditions. The progress of the dissolution was followed by bulk chemical analysis of the slag composition as a function of time; no metallographic examination is reported. The authors report in almost all experiments " the rapid introduction of chromium from the cylinder into the slag phase within the first 15 min.".

Ringdalen [8] examined the reduction of (90% -300 μm) Turkish fine chromites with coke, with quartz and bauxite flux additions. The target slag at full reduction was $40\%MgO-26\%Al_2O_3-34\%SiO_2$ having a liquidus temperature of 1973K. Electron microprobe X–ray analysis of the samples demonstrated an initial increase in chromium concentration in the bulk slag phase up to at least $8wt\%^oCr_2O_3$. The chromium concentration of the bulk slag was subsequently progressively lowered through chemical reduction to less than $0.5wt\% Cr_2O_3$ in less than 50 min. The initial dissolution of chromium into the slag phase is clearly rapid compared to the reduction reaction. In spite of this initial rapid dissolution of the chromite, the spinel particles were not completely dissolved even after 5 hours reduction. Ringdalen [8] also observed that the presence of excess carbon, generating lower oxygen partial pressures, results in faster reduction of Turkish fines chromite.
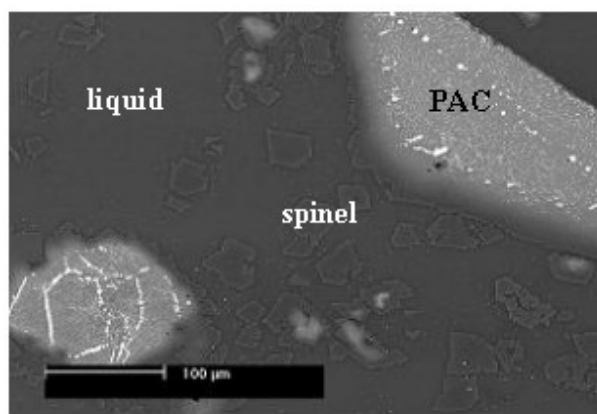
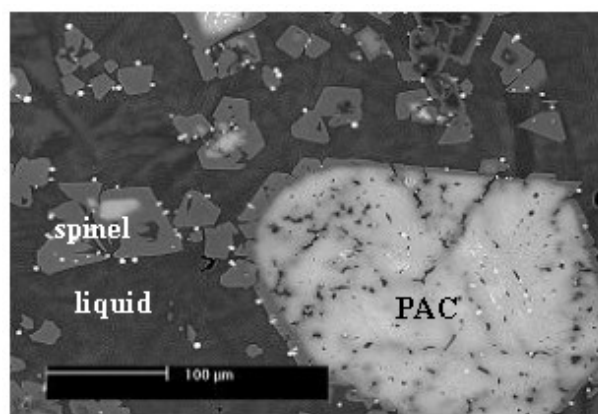Figure 6. Ferrochromium smelting slag at 1873K containing undissolved, partially altered chromite (PAC).

Figure 7. Ferrochromium smelting slag "slow cooled" from the furnace showing the precipitation of secondary spinel.

Phase equilibrium studies relevant to chromium smelting are listed in references [37-62]. Although the dissolution of chromium oxide under oxidising conditions is limited (Cr_2O_3-MgO-SiO_2 in air, [56], Cr_2O_3-SiO_2-Al_2O_3 in air, Degterov and Pelton [54]), under reducing conditions, approaching chromium metal saturation the solubility of chromium oxide in slag is greatly enhanced. (CrO_x-MgO-SiO_2 Cr metal saturation, Slag Atlas [56]; CrO_x-CaO-SiO_2, Muan [50]; CrO_x-CaO-MgO-Al_2O_3-SiO_2, Morita et al [52]; CrO_x-MgO-Al_2O_3-SiO_2, Kossyrev et al [55]; CrO_x-SiO_2-Al_2O_3, Degterov and Pelton [54]).

For slags from which chromium has been reduced, the slag system is represented most simply by the ternary system MgO-Al_2O_3-SiO_2 [56]. A feature of this diagram is the primary phase field of the refractory spinel MgO.Al_2O_3. Within this primary phase field the liquidus temperature of 1873K appears to be not greatly dependent on the MgO/Al_2O_3 ratio in the slag. Approximately 40wt% SiO_2 in this ternary would ensure that the slag is completely liquid at 1873K for slags with MgO/Al_2O_3 mol ratios of unity. Yonggao [57] reports the melting points of MgO-Al_2O_3-SiO_2 slags between 30-40wt% SiO_2 and MgO/Al_2O_3 = 0.8-2.8 however no information is provided on the technique used to determine these values.

Most industrial slags also contain lime flux of various proportions. The liquidus surfaces for the system CaO-MgO-Al_2O_3-SiO_2 quoted in "Slag Atlas" [56] and "Phase Diagrams for Ceramists" [42] are principally derived from the work of Osborn et al. [38]. Liquidus temperatures in the system Cr_2O_3-CaO-MgO-Al_2O_3-SiO_2 in air have been reported for selected sections, (Berry et al. [38]; El-Shahat and White [43-45]; Biggar and O'Hara [46]; Biggar [47,48]; Onuma and Tohara [49]; Segadaes and Brett [51]. These studies are principally focused on composition areas and reactions occurring in the production of chrome-magnesite refractories.

In submerged arc smelting practice, if complete dissolution of the chromite grains does not take place in the hot zone (Zone 4) then it is unlikely that significant further reduction will occur in the furnace. The argument here is that as the slag moves away from the electrodes there is a decrease in slag temperature. The slag tapping temperatures (approximately 1873K) are below those in the coke bed. If the slag is already saturated with the spinel MgO.Al_2O_3 in the coke bed then cooling will lead to further precipitation on the existing solid surfaces, which act as heterogeneous nucleation sites for the precipitate phase. The formation of these secondary spinels on the surfaces of the PACs and the partial crystallisation of the melt is illustrated in the micrograph of the tapped slag shown in Figure 7.

As indicated above the solubility of chromium oxide in slag increases with decreasing oxygen partial pressure. Chromium can exist in slag solution as Cr^{6+}, Cr^{3+} and as Cr^{2+} [58-62]. Xiao et al. [62] recently reviewed the data available on the Cr^{3+}/ Cr^{2+} ratios in molten CrO_x-CaO-SiO_2 slags for a range of slag compositions and oxygen partial pressures. Xiao and Holappa [59] has used a regular solution thermodynamic model to estimate the CrO and Cr_2O_3 activities in a range of slag compositions at 1873K.

2.3 Reduction of chromium from the slag by solid carbon

Once in solution in the slag the chromium can be reduced by carbon to form metal alloy or carbide [63-78].

The effects of silica on the kinetics of reduction of friable Zimbabwean chromite ore (65% - 600 μm) with fine coke (-500 μm) at temperatures between 1623 and 2023K have been investigated by Taneka and Robertson [64]. The extent of reaction was followed by measuring the total gas volume produced by the reaction as a function of time. At reaction temperatures of 1923 and 2023K, complete reduction was achieved within ten minutes. Residual chromium in the slag was quoted as 0.3 to 2.7wt% Cr_2O_3. Silica reduction from the slag was also observed to occur at these high temperatures.

Fukagawa and Shimoda [67] reduced sintered fluxed South African chrome ore in graphite crucibles at 1923K. A range of CaO/SiO_2 mixtures, which were used as fluxes, from 0.6 to 1.63 were investigated. The reaction rates were calculated based on observations of slag erosion of the carbon crucibles following the experiments. On this basis the rates at $CaO/SiO_2 = 0.6$ appeared to be low, but as the authors point out this also corresponded to foaming of the slag during reaction. Slag foaming could be interpreted as indicative of a vigorous reaction; the foaming may also be due to the higher viscosities of these slags. The samples reduced using flux containing $CaO/SiO_2 = 1.63$, and MgO for $CaO/SiO_2 = 1.1$, gave significantly lower reaction rates particularly at greater extents of reaction.

Shimoo et al [68,69] investigated the reduction of iron-free CaO-SiO_2-Cr_2O_3 and CaO-Al_2O_3-Cr_2O_3 slags with graphite between 1773 and 1973K. In these cases, chromium carbides have been observed to form on the surfaces of carbon particles. They observed that the rate of reduction increased significantly with the formation of carbide product layer on the carbon surface. The formation of carbide also resulted in the increased wettability of the solid surface by the slag. The reduction rate varied significantly with composition of the CaO-SiO_2 slag.

The reduction of $(Fe,Mg)O.Cr_2O_3$ spinels in CaO-SiO_2 slags was also studied at 1873K by Shimoo et al. [71]. The reduction of iron from the spinel was found to precede the reduction of the chromium. The reduction of chromium from the binary CaO - SiO_2 slags was found to be relatively slow as a result of poor slag/C contact. The presence of MgO and/or Al_2O_3 considerably improved the wettability of the slag and the reaction rate.

Pei and Wijk [72] report the reduction of chromium oxides from iron-free CaO-MgO-Al_2O_3-SiO_2 slags using 14mm ID graphite crucibles. Initial reactions result in the reduction of Cr^{3+} in the slag to Cr^{2+}; further reduction resulted in the formation of chromium carbide. Below 1798K solid Cr_3C_2 is observed to form at the slag/carbon interface, above 1823K the reduction product is liquid Cr-C alloy. Reduction of initially 1.2wt% Cr_2O_3 to less than 0.2wt% Cr_2O_3 was achieved within 10 minutes at 1923K, and it was argued that the rate was limited by mass transfer in the slag phase.

The effects of silica addition on the kinetics of reduction of Greek chromites at 1573 and 1673K using graphite powders have been studied by Lekatou and Walker [75]. Chrome metallisation in these tests did not exceed 80% and no systematic study was carried out on the effects of slag chemistry.

Gornerup and Lahiri [76] studied the reduction of chromium from CaO/SiO_2 slags in graphite crucibles at temperatures from 1723-1973K. The synthetic slags contained initially 5wt% chromium in solution, and CaO/SiO_2 ratios from 0.8 to 2.0 were investigated and the liquidus temperatures were determined to be less than 1673K. At temperatures above the melting temperature of metallic iron, complete reduction of iron and chromium from the slag was reported within 20 minutes of the start of the experiment. Iron and chromium concentration profiles in the slag phase adjacent to the crucible wall, determined by electron probe X-ray microanalysis, indicated that the rates were limited by slag phase mass transfer.

Kucukkaragoz et al. [77] and Vadar and Eric [78] investigated the reduction of South African chromite ores entrapped in slag in an inductively heated graphite crucible. Dip samples of slag were taken during reaction and bulk chemical analysis performed. The effects of slag composition on rate of reduction are reported for a range of slag chemistries at 1873K.

The effect of carbon type on the rate of reduction of chromium from slags does not appear to have been systematically studied. Dijs and Smith [65] examined the use of carbons and coke up to 1773K; they found that carbons with higher CO_2 reactivity gave faster rates of reduction of the slag.
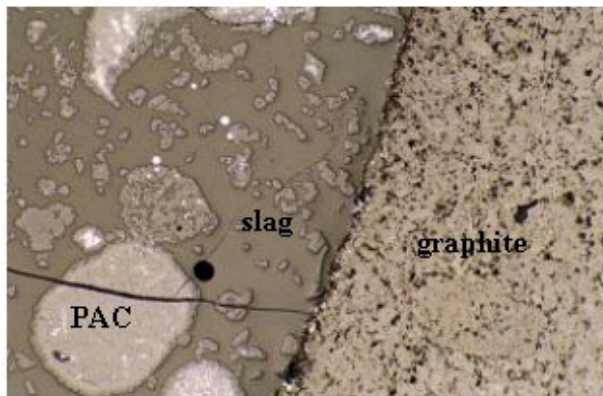

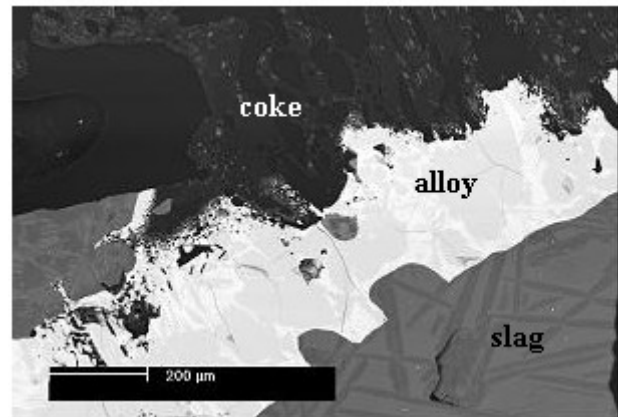Figure 8. Micrograph showing the interface between ferrochomium smelting slag and graphite.

Figure 9. Micrograph showing the interface between ferrochomium smelting slag, coke and alloy.

2.4 Reduction of chromium from the spinel by carbon in molten alloy

Demir and Eric [81]; Uslu and Eric [82]; Eric [85] investigated the reduction of solid chromite by carbon in Fe-Cr-C alloys using a rotating cylinder technique. The extent of reaction was followed by measurement of changes in the alloy composition with reaction time. Experiments were carried out between 1773 and 1953K and carbon concentrations of 4, 5 and 7wt%. Examination of the partially reduced samples after 30 minutes reduction revealed the formation of a $(Cr,Fe)_7C_3$ carbide layer that covered the reaction interface. The presence of this solid product layer leads to a significant decrease in the rate of reduction of the spinel. The overall rates of carbon decrease in the alloy were reported but these data were not translated into apparent interfacial reaction rates.

2.5 Reduction of chromium in solution in slag by carbon in molten alloy

Yokoyama et al. [89] reported a series of experiments examining the reduction of chromite ore with Fe-Si-C melts in graphite crucibles at temperatures between 1743-1903K. The yield of chromium was increased with the use of high lime fluxes, which were used to dissolve the South African chromite. The reaction was followed over the reaction time by chemical analysis of slag samples. From results indicating variations in rate with slag chemistry and the continued presence of undissolved chromite it was concluded that the rates were limited by mass transport in the slag phase under these conditions.

Pei and Wijk [89,90] studied the reduction of Zimbabwean chromite ores in Fe-C melts in graphite crucibles at 1903K. The chromite was dissolved in $CaO-SiO_2$ slags but the effects of MgO and Al_2O_3 additions were also examined. In the case of $CaO-SiO_2$ slags, the chromium oxide concentration of the slag was observed to initially increase, reaching a maximum value of approximately 3wt% within 10 minutes; complete dissolution and reduction of chromium oxide from the slag was achieved within 20 minutes. The addition of MgO and Al_2O_3 resulted in significant decreases in the maximum chromium oxide concentration observed in the slag and greatly reduced overall reduction rates.

The reduction of Zimbabwean chromite ores by Fe-C melts was also studied by Tsomondo et al [93]. The total chromium concentration in the $CaO-SiO_2$ based slag was monitored as a function of reaction time at temperatures in the range at 1853-1913K. The reduction kinetics were described by a first order rate equation with respect to the chromium concentration in the slag. The initial reaction rates were observed to be rapid in all cases, however, the residual chromium in the slag was found to increase with decreasing basicity from 1.5 to 0.5.

Following earlier studies of the reduction of chromium from slags in graphite crucibles Gornerup and Lahiri [94, 95] added Fe and Fe-C powders to the slags at 1873K; the result was a dramatic increase in reaction rate accompanied by severe foaming.
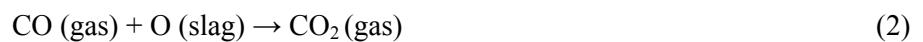
Nakasuga et al. [96] studied the rate of reduction of chromium from Cr_2O_3-CaO-MgO-SiO_2-Al_2O_3-CaF_2 slags with carbon in molten Fe-C alloys at 1773 and 1873K. The reduction rate was such that "almost all of the Cr_2O_3 was reduced from the slag within 10 minutes". The rate of reduction was found to increase with increasing CaF_2 addition; this effect is attributed to the decrease in slag viscosity accompanying these additions.

It is now widely accepted that the reaction mechanisms between slag and carbon in alloy involves a two-step process with the formation of a gas film at the slag/alloy interface [87,91,92,94].

Carbon gasification from the alloy

$$C \text{ (in alloy)} + CO_2 \text{ (gas)} \rightarrow 2CO \text{ (gas)} \tag{1}$$
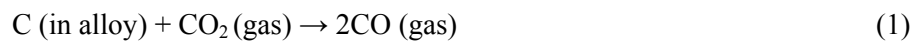
Gaseous reduction of the slag

$$CO \text{ (gas)} + O \text{ (slag)} \rightarrow CO_2 \text{ (gas)} \tag{2}$$

The so-called gas ferrying mechanism is shown in Fig. 10. It has been established that the chemical rates of carbon gasification from the alloy surface are at least an order of magnitude greater than from solid carbon (Sain and Belton, [86]). To retain the alloy as liquid and to ensure an adequate supply of carbon for reaction (1) the rate of dissolution solid carbon into the alloy should also be rapid. The rates of carbon dissolution in metal have been shown, to be dependent on carbon type [98].

The relative contributions of gasification via solid carbon and carbon dissolved in alloy to the overall reactions will depend on the surface areas of carbon and alloy at the carbon/slag interface, CO_2 reactivity and carbon dissolution rates in alloy [97].

The reaction mechanisms at the carbon surface can also influence the gas evolution from these surfaces. The slag phase generally does not wet the carbon surface [Fig.8], but it has been observed to wet the molten alloy [Fig.5 and 6]. If the gasification occurs between solid carbon and the gas phase the product gas will accumulate into relatively large gas bubbles before becoming detached from the carbon. Gasification at the metal surface, although faster, has been shown [97] to produce relatively fine (1mm diameter) bubbles, which have a tendency to form stable slag foams.

The selection of the optimum carbon type for use in submerged arc processes remains an area of interest for commercial practice.
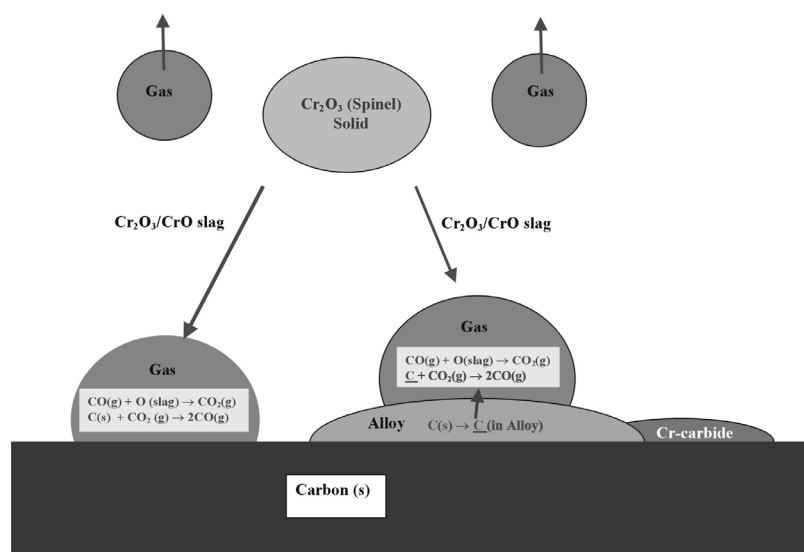

Figure 10. Summary of reaction mechanisms occurring in the lower furnace
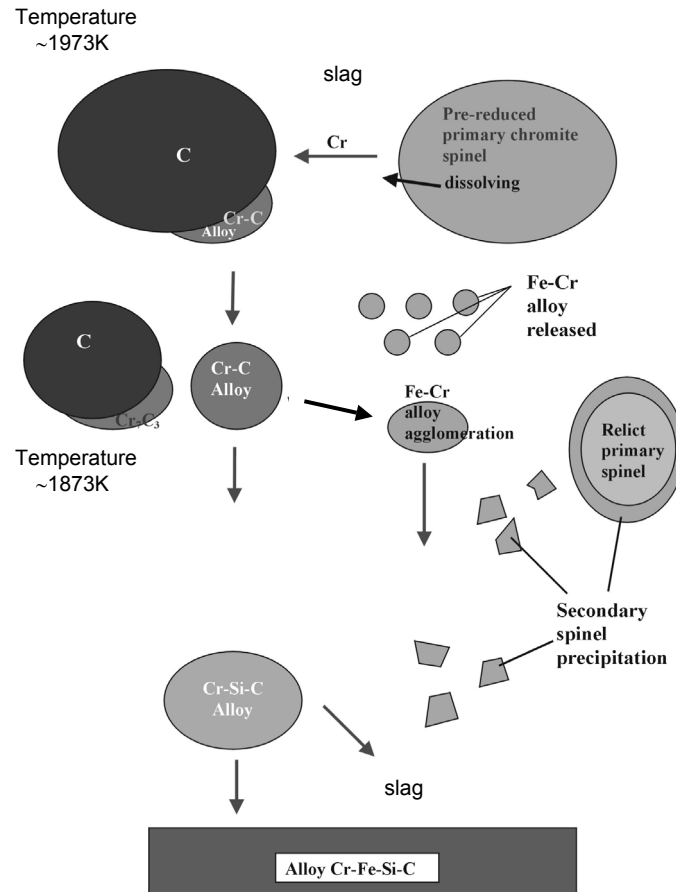during submerged arc smelting of ferrochromium.

Figure 11. Alternative reaction pathways for reduction of ferrochromium slags with carbon.

3. SUMMARY

As chromite ore moves through the submerged arc furnace during processing it passes through a number of reaction zones.

In the upper furnace, zone 1, the chromite particulates are present as "loose charge" and product gas from the lower furnace consisting of principally CO and CO_2 passes through this packed bed. Reactions between the gases and the solid chromite result in the partial reduction of the chromite and the formation of iron and chromium alloy, and in some cases metal carbides.

In the lower furnace, zones 2-6, a series of reaction steps take place involving the slag phase (Fig. 11):
- Dissolution of chromite spinel in slag
- Reduction of the slag phase to form alloy
- Alloy/slag separation

Although the overall reaction is described by the removal of oxygen by solid carbon, this reaction can take place through a number of pathways involving; carbon monoxide formation from solid carbon or carbon dissolved in alloy; reaction of CO gas with slag; metal ion diffusion in the slag phase.

Each of these mechanisms contributes to the overall recovery of chromium as alloy. Optimisation of the process to enhance the rates and extent to which these reactions proceed, and to maximise recovery, production rate and energy efficiency is assisted by improved understanding of the various reactions and reaction mechanisms operative in the process, and by taking action through feed selection and preparation, and adjustment of process conditions.

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