A Laboratory Investigation of the Smelting Mechanisms Associated with the Production of High-carbon Ferrochromium

by R.C. URQUHART*, P.R. JOCHENS*, and D.D. HOWAT† (presented by Dr Urquhart)

SYNOPSIS
A new technique – a variation of the SCICE (stationary charge in controlled environment) technique – was used in the study. A large sample (4kg) was employed, and the rates of reduction of both the iron and the chromium from the chromite ore were measured. It was shown that, at temperatures up to 1500°C, reduction of the chromite ore is controlled by the diffusion of iron and chromium ions in the chromite spinel. At 1500°C, the reduction rate of chromium from the chromite spinel is increased by the fluxing reaction. In the presence of slag, at temperatures higher than 1500°C, the reduction of chromite ore by carbon is rapid. It was found that these mechanisms of reduction are not independent of one another but have to occur in the order described.

INTRODUCTION
It was believed that very useful information about the behaviour of the burden components during smelting to high-carbon ferrochromium would be obtained from an accurate laboratory study of a sample large enough to be representative of the material used in a plant and of comparable particle size. The approach used is a variation of the technique known as 'stationary charge in controlled environment' (SCICE)1,2. A representative vertical section of the furnace is used to contain the vertical descent of the burden, and, as smelting progresses, the burden settles slowly from the first level through to the slag layer, being subjected to increasing temperatures as it descends through the furnace. The problem of the composition and flowrate of reducing gas (such as carbon monoxide, which would occur in a blast furnace) can be ignored owing to the relative immunity of chromite ore to reduction by carbon monoxide. As the rate of descent of the burden in the submerged-arc furnace is not well known, the element was treated at a selected temperature for varying periods of time and then at temperatures varying between 1200 and 1800°C.

The particle sizes of the material normally charged to a submerged-arc furnace are in the following range:
- ore 25 to 100 mm
- flux 50 to 100 mm
- char 25 to 50 mm.

The following size ranges were chosen for these experiments so that they would correspond to the particle-size relations encountered in a plant and so that there would be at least 15 packing diameters:
- ore 3.2 to 12.7 mm 70.3 per cent
- flux 6.3 to 12.7 mm 14.0 per cent
- char 3.2 to 6.3 mm 15.7 per cent.

The composition of the charge was calculated according to the methods used in industrial practice, except that coal char additional to the stoichiometric amount was not used. The starting materials were typically South African in composition (chromite ore having a CaS content of 43 per cent and a chromium-to-iron ratio of 1.58, and coal char having a fixed carbon content of 79.3 per cent).

EXPERIMENTAL APPARATUS AND PROCEDURE
SCICE charges, each 4 kg in mass, were placed in a graphite crucible, 200 mm high and of 150 mm internal diameter. The crucible was heated in a Birlefco 40 kHz induction furnace at a heating rate of 400°C per hour. The temperature was monitored by two thermocouples immersed in the burden, one at the centre of the crucible and the other at the crucible wall. For temperatures up to 1600°C, Pt—6%Rh/Pt—30%Rh thermocouples were used, and, for the experiments at 1700 and 1800°C, Pt—20%Rh/Pt—40%Rh thermocouples were preferred. Special precautions were necessary to protect these thermocouples from the severe reducing conditions and from attack by the slag.

Once the 4 kg sample had been heated to the desired temperature and maintained at this temperature for the required time, the furnace power was turned off and the charge was allowed to cool to room temperature. The rate of cooling depended on the initial temperature of the sample. Between 1400 and 1300°C, the cooling rate was 8°C/min. The error introduced by this quenching procedure is small and is allowed for by the test done for 'zero hours'. This initial test consisted in heating of the sample to the required temperature and immediate cooling to room temperature. Each subsequent sample, i.e. 1, 2, 4 hours, etc., was cooled from the same temperature and under the same conditions – therefore at the same rate.

Samples treated at temperatures of 1200, 1300, and 1400°C were easily removed from the graphite crucible because little melting had occurred. These samples were riffled into two portions.

One portion was ground in a porcelain ball mill for one hour to give a grading analysis of 90 per cent smaller than 100 mesh. It was then leached in boiling 10 per cent (by volume) sulphuric acid, and the filtrate was analysed for iron and chromium by atomic-absorption spectrophotometry. (Chromite ore is insoluble in dilute acid, whereas iron, alloys of iron and chromium, and their carbides are soluble.) Samples that had been heated to 1500°C contained a large amount of metallic beads, which were removed by hand-picking after the samples had been crushed through rolls. The metallic beads were weighed and analysed for...
iron, chromium, silicon, and carbon. The remaining portions of the samples were ball-milled and then leached. In all instances, three different portions of each sample were leached and the mean result taken.

**QUALITATIVE OBSERVATIONS OF THE CHARGE AFTER HEATING**

Visual examination of the crucible contents after being sectioned reveals that there are three distinct stages in the process of chromite-ore reduction: relatively little reaction and no visible change in the burden, incipient fusion and extensive reduction, and separation into a layer of alloy and slag. The crucible contents in all tests conducted at 1100, 1200, and 1300°C were visibly similar in that little reaction or sintering occurred. Longer residence times at 1500°C resulted in some considerable degree of incipient fusion and decrease in bulk, whereas, at 1600°C, the sections reveal faster reaction rates and separation into a slag and alloy layer. Reaction and separation at 1700 and 1800°C were more rapid than at 1600°C.

Continuous heating of the charge resulted in no visible change (aside from volatiles being driven from the coal char) until 1400°C, when evolution of a grey fume was observed. At 1500°C, the fume evolution was much increased and temperature control became difficult (the difference between the temperatures at the crucible wall and at the centre had started to increase). The power needed to maintain the temperature was increasingly high owing to endothermic-reduction reactions.

The initial stage in the reduction of chromite spinel is the transformation of Fe$^{3+}$ to Fe$^{2+}$. Because of the low R$_2$O$_3$-to-RO ratio of the Transvaal chromite used (0.87), this transformation is slower than it would be for a Russian chromite ore (1.75). In these tests, the Fe$_2$O$_3$ content of the ore decreased from 7.5 per cent to nearly zero over the temperature range 500 to 1400°C.

---

**Figure 1**

Polished sections of chromite ore

1. As received from the mine. The light-coloured grain of chromite spinel is surrounded by the darker-coloured cementing gangue X45.
2. As received from the mine, showing the different sizes of chromite spinel grains. X23.
3. Reacted at 1200°C for 1 hour. The initiation of reaction is shown by the white alloy beads. X45.
4. Reacted at 1200°C for 4 hours. Alloy beads are concentrated in cracks in the spinel and in grain boundaries. The diffuse (darker) zone is just evident at the reacted edges of the chromite grains. X45.
5. The edge of a particle of chromite ore after 1 hour at 1300°C. Reduction at the exterior of the particle is fairly pronounced. X45.
6. A particle of chromite ore reacted at 1300°C for 4 hours. Decrepitation and possible melting of the darker gangue is apparent. X45.
Figure 2

Polished sections of chromite ore

1. The edge of a chromite particle that has been heated to 1400°C and then cooled. The small alloy beads of the lower reaction temperatures have begun to coalesce. X65

2. An example of reduction at 1400°C. The gangue inside the particle of chromite ore has been in a molten state. X65

3. The mechanism of sintering of two chromite particles (1400°C). Two particles that are fairly rich in gangue have been 'welded' together by the flow of their molten gangue. X65

4. A typical alloy obtained from the settled metal layer at 1700°C. The white region is (Fe,Cr)$_3$C$_6$, the dark region is a solid solution of iron and chromium, and the small phases present inside the dark phases represent a eutectic of iron—chromium solid solution and carbide. X65
The changes undergone by the chromite ore are best illustrated by photomicrographs of polished sections of chromite particles taken from the SCICE experiments. The chromite ore as received from the mine is shown in Figure 1, 1 and 2. The light-coloured chromite-spinel grains are surrounded by darker cementing gangue.

Figure 1, 3 and 4 show areas near the edge of a particle of chromite ore taken from an SCICE charge reacted at 1200°C. It is apparent from the position of the white metallic beads that diffusion of the reducing agent along the grain boundary is rapid compared with bulk diffusion. The chromite particle of Figure 1, 4 shows the darkened, diffuse zone at the circumference of the chromite-spinel grain where reaction has occurred. Electron-microprobe analysis showed that this zone is depleted of iron.

Particles of chromite ore removed from a burden that had been reacted at 1300°C (Figure 1, 5 and 6) show an increase in the amount of metal produced, especially at the edge of the ore particle. At this temperature, reduction has occurred all round the surface of the chromite-ore particle, which suggests that surface diffusion by the reducing agent is rapid.

Figure 2, 1 and 2 represent a chromite ore reacted at 1400°C, and Figure 2, 3 illustrates the mechanism for sintering at 1400°C between two chromite-ore particles. A section of the sample shown in Figure 2, 3 was examined with the electron microprobe. A scan was made from the midpoint of one chromite-spinel grain to its circumference, across the gangue phase to the circumference of a second chromite-spinel grain, and then to the middle of the second grain. The concentrations of iron and chromium were determined and are plotted for their probable oxide forms in Figure 3.

Figure 2, 4 shows a typical alloy from the settled metal layer at 1700°C. The analyses of the alloys showed that, at lower temperatures, the iron is preferentially reduced because the iron-to-chromium ratio is very high. This ratio decreases with increase in temperature and with time at any particular temperature. Only at temperatures of 1600°C and above were the expected chromium-to-iron ratios obtained. The carbon content was above 5.5 per cent for all temperatures from 1500°C and higher, and the silicon content increased with both temperature and time above 1600°C. The graphs of Figure 4 suggest that the carbon contents of the metal beads approach the solubility limit.

The mechanism of slag formation is illustrated in Figure 5. Figure 6 portrays the dissolution of the chromite-spinel grains in the slag phase at 1600 and 1700°C. No chromite grains were found suspended in the slag obtained from experiments conducted at 1800°C. Slag analyses indicated that the MgO-to-Al₂O₃ ratio decreased from 8.84 at 1500°C to 0.75 at 1800°C. The SiO₂ content decreased from 50.6 to 42.4 per cent over the same temperature interval.
Polished sections illustrating the mechanisms of slag formation

1. Chromite grain dissolving in slag at 1600°C. The outer edge of the chromite grain is deficient in both iron and chromium ions. X65

2. Chromite—slag interface at 1600°C. Dissolution is enhanced by erosion of the attacked portion of the chromite grain by slag. X65

3. Severe attack on a chromite particle by the dissolving slag (1600°C). X65

4. The last stages of dissolution of a chromite grain in metallurgical slag at 1700°C. X65.
Polished sections showing the dissolution of the chromite spinel grains in the slag phase at 1600 or 1700°C

1. The active role played by the gangue as far as the initiation of slag formation. The gangue of two chromite particles has begun to flow at 1400°C. X65.

2. Incipient slag formation at the point of contact between a quartz particle and a chromite particle (1500°C). X65

3. The interface between a quartz particle (lower) and a primary slag rich in chromite particles (upper) at 1500°C. X65

4. The crystal phases present after a slag has been cooled. The sections were taken from the slag layer of a sample reacted at 1600°C. The long, needlelike phases are forsterite (MgAl₂O₄), and the matte-type phases collected in the centre of the figure are spinel (MgAl₂O₄). The tiny metallic beads are an exsolution product, probably resulting from the reaction 3CrO₃ → Cr + Cr₂O₃ during cooling. X65.
RATE OF REDUCTION OF CHROMITE ORE

The rate of reduction of chromite ore to metallic iron and chromium is plotted in Figures 7 and 8. The rates of reduction at 1700 and 1800°C are not included, because the large amount of heat absorbed by the reduction reactions made it impossible for these temperatures to be reached at the chosen rate of 400°C per hour. One sample was reacted at 1500°C without the addition of a quartz flux, and pieces of alumina thermocouple tubes were included in the burden to preserve a spacing equivalent to that of the previous heats. The absence of a quartz flux meant that slag did not form at 1500°C, and this sample is therefore similar to the samples reacted at 1200, 1300, and 1400°C, in that slag formation was prevented.

Figure 7
The fraction of the iron contained in the chromite ore that was reduced in the SCICE experiments

Figure 8
The fraction of the chromium contained in the chromite ore that was reduced in the SCICE experiments
The rate of reduction of iron from the chromite ore was not affected by the presence of quartz, but chromium was produced at a considerably increased rate in the presence of a quartz flux at 1500°C. As found by Kadarmetov⁸, the reduction of the chromite ore — both the individual rates of reduction of iron and chromium from the chromite ore and the total rate of reduction — occurred at a decelerating rate. Various equations relating to rate-controlling processes were applied to the results. The equations that came nearest to fitting the results were based on the solid-state diffusion of the reacting species through a product layer. However, because the rate constants determined were not constant for the various reaction times, the results for the reduction of iron and chromium from chromite ore were plotted in Arrhenius plots.

The reduction of iron from chromite ore satisfies the expression

\[ x = 236,1 + 151,1t - 21.09t^2 + 1.122r^3 \exp \left[ \frac{24200}{RT} \right] \]

where \( x \) = degree of reduction of iron from chromite ore, \( t \) = time in hours, and \( T \) = absolute temperature in kelvins.

The above expression has been advanced by Erofeev⁹ to describe a topochemical reaction that starts simultaneously on the faces of all cubic (chromite spinel) crystals. The constants were determined by minimization of the squared errors according to a method devised by Powell¹⁰. The true activation energy for reduction cannot be calculated from these results, but an apparent activation energy, expressed in cal/mol, can be obtained to express the algebraic sum of the activation energy of the rate-determining steps of the reaction and the heat terms determined by changes in the properties of the system with temperature. In fact, Themelis and Gauvin¹¹ remark that the term ‘temperature coefficient’ is more appropriate than ‘activation energy’ to denote the combined effects of temperature on both the physical and chemical phenomena associated with reduction. The temperature coefficient for the reduction of iron from the chromite ore was calculated as 24.2 ± 0.4 kcal/mol in the temperature range 1200 to 1500°C. That for the reduction of chromium varies from about 75 kcal/mol at 1200°C to about 25 kcal/mol at 1500°C. From comparison of these values with the activation energies for diffusion in spinel lattices¹², it appears that diffusion of iron and chromium in the chromite spinel is the rate-limiting step.

**EFFECT OF THE DISSOLUTION OF CHROMITE ORE IN SLAG ON THE RATE OF REDUCTION OF CHROMITE ORES**

The SCICE experimental results for the reduction of chromite ore at 1500°C indicate that chromium is produced more rapidly when a slag is formed. The fluxing action of silica on the chromite spinel, as shown in Figure 5, offers a partial explanation for this phenomenon. If the rate of reduction of chromate ore increases in the presence of slag, and if carbon is the only reducing agent added to the system (gaseous reducing agents such as CO and SiO₂ were shown to be ineffective), the path for reduction at these temperatures must be predominantly via the slag phase.

Boronenkov et al.¹³ measured the kinetics of the reduction of iron and chromium from high-carbon ferrochromium slags. Thermogravimetric analysis was used, and the slags were reduced in a graphite or alumina crucible, with carbon-saturated ferrochromium as the reducing agent. The authors found that, at high chromic oxide contents of the slag (more than 6 per cent), the reduction of chromium from the slag is controlled by the process of carbon oxidation and desorption of the carbon monoxide from the system, whereas, at low concentrations of chromic oxide in the slag (less than 2 per cent), the reaction is retarded by the diffusion of chromium ions in the slag. The high chromic oxide contents of some of the slags that were used (Cr₂O₃ 15 and 20 per cent) indicate that these slags could not have been above liquidus temperature at 1600°C⁴. Thus, although the slags containing small amounts of chromic oxide were above their liquidus temperatures and the chromic oxide was in solution, at 1600°C the slags rich in chromic oxide probably were not. This may be the reason for the change in mechanism at high chromic oxide contents in the slag. Van der Colf¹⁵ reduced, in a graphite crucible, slags containing Cr₂O₃ and found that the reaction was rapid.

**Experimental Investigation**

Two series of experiments were done:
1. the dissolution of chromite ore into a slag, and
2. the simultaneous dissolution of a chromite-ore particle into a slag and reduction of the dissolved iron and chromium oxides from the slag by carbon.

The following typical primary slag was used in the experiments:
- MgO 21.43 per cent,
- Al₂O₃ 28.57 per cent, and
- SiO₂ 50.00 per cent.

The physical properties of these slags have been determined by Johnston¹⁶. Preliminary tests on a pure, unreduced chromite dissolved in a slag at 1500°C showed that dissolution of the refractory spinel structure is exceedingly slow. Thus, in the dissolution experiments, a partially reduced chromite, which is more representative of conditions in a submerged-arc furnace than an unreduced chromite, was used.

Fifty cubes of chromite ore were reacted in contact with graphite powder by being heated in a graphite crucible at 400°C per hour to 1400°C and maintained at 1400°C for 1 hour. The samples were examined for homogeneity under an optical microscope. The amount of reduction that had occurred was 6.64 per cent in the iron and 0.63 per cent in the chromium, where 100 per cent refers to complete reduction of each of these metals from the chromite ore. Because a cube (edge length 1.2 cm) could be cut with relative ease by use of a diamond wheel, this was the geometry adopted.

The experimental procedure involved melting of the slag in a graphite or molybdenum crucible (depending on whether the experiment was to determine dissolution and reduction or only dissolution) at the experimental temperature in an atmosphere of argon. The cube of chromite ore was suspended in 25 g of molten slag by means of a 1 mm-diameter molybdenum wire fixed in a four-bore alumina thermodouple tube. Experimental times in the combined dissolution and reduction tests at higher temperatures were necessarily short owing to attack of the molybdenum wire.

The slag from the dissolution experiment was analysed for FeO, Cr₂O₃, MgO, Al₂O₃, and SiO₂. All of the slags obtained from the dissolution and reduction experiments were leached in 10 per cent (by volume) sulphuric acid so that the amount of iron and chromium reduced from the chromite-ore cube could be determined.

The rate of dissolution of the chromite-ore cube was
assumed to be controlled by diffusion of the dissolving oxides in the slag phase. For the conditions of the dissolution experiments, the rate of dissolution depends on the square root of time.

The dissolution curves (Figure 9) appear to be linear during the initial stages of dissolution, which tends to confirm the prediction that the dissolution of iron and chromium oxides from the chromite ore into the slag is controlled by the diffusion of Fe"" and Cr"" away from the interface into the bulk of the slag. The deviation of the plots from linearity at increasing dissolution times indicates that the bulk concentration is no longer zero but some finite value. The reason for the fall in the diffusion flux at increased dissolution times is that most of the slags were then below their liquidus temperature and, as a result, were saturated with iron and chromium oxides.

A dissolving chromite-ore cube when examined by microscope displays a dark region at the edge of the chromite-spinel grain. This region is depleted in iron and chromium ions as shown by an electron-microprobe scan. Segments of this region float into the bulk of the slags as dissolution progresses, revealing fresh chromite rich in iron and chromium ions to the corroding slag. Thus the diffusion of iron and chromium ions from the chromite interior to the interface would not retard the dissolution process.

**Rate of Reduction of Chromium Ore via a Slag Phase**

The data obtained by the simultaneous dissolution of a chromite ore into slag and the reduction of the dissolved iron and chromium oxides with carbon are plotted against the square root of time in Figure 10. If the graphs of Figure 9 are compared with the graphs of Figure 10, it becomes evident that the rate of reduction of iron and chromium from the slag is higher than the rate of dissolution of the iron and chromium oxides into the slag. If the rate of reduction of a chromite ore via a slag phase is controlled by the rate of chromite dissolution into the slag and diffusion to the graphite wall of the crucible, then the rate of reduction should equal the rate of dissolution. During reduction, the carbon monoxide produced rises through the slag, causing a stirring action in the slag, which was especially pronounced at 1580 and 1620°C. This stirring action, which has been observed by other authors who studied the rate of removal of FeO from slags, may be responsible for the change in the mechanism of dissolution from a first-order process to one of a higher order. The order of the reaction was found to approach 2 during active bubbling in the slag.

The unusually low rate of the reduction of chromium by this mechanism at 1500°C suggests that the reaction at this temperature may be rate-controlled by a chemical reaction. However, it is apparent from the SCICE experiments...
In Figure 10, the amount of iron and chromium reduced from a chromite-ore cube that was suspended in a slag contained in a graphite crucible.

that the reduction of both FeO and Cr₂O₃ is relatively rapid at 1500°C, and it was shown that the presence of SiO₂ enhanced the reduction of Cr₂O₃. Therefore, at this temperature, it is not the mechanism by which chromite ore dissolves in slag that controls the rate of reduction of Cr₂O₃. If the standard free energies for reduction of MgCr₂O₄ with solid carbon are considered, it will be realized that they are lower when the reaction occurs in the presence of SiO₂ so that a magnesium silicate slag phase, an alloy, and carbon monoxide are formed.

CONCLUSIONS

The SCICE experiments provided visual information on the smelting process by permitting samples of the reactants to be examined microscopically after they had been subjected to known thermal conditions. The major observations were that the reduction process of the chromite ore by solid char is initiated at the surface and progresses inwards, and that this reduction is accompanied by diffusion of the iron and chromium to the surface of the chromite ore. It was also shown that, at temperatures of 1600°C and higher, the grains of chromite spinel can dissolve in the molten-slag phase.

Analysis of the alloys and slags produced at the various temperatures indicates that the carbon contents of the alloys approach the solubility limit at lower temperatures. The slags are initially high in SiO₂, and, with increase in temperature, the MgO and Al₂O₃ contents increase. A feature of the slag analyses is the low FeO and Cr₂O₃ contents.

The reduction of iron from the chromite ore satisfies an expression that describes a topochemical reaction starting simultaneously on the faces of the cubic crystals. However, the reduction of chromium from the ore does not follow a unique mechanism over the temperature range investigated.

Examination of the dissolution of chromite ore in the slag as part of the reduction process showed that the dissolution of iron and chromium oxides from the chromite ore into the slag is controlled by the diffusion of iron and chromium ions away from the interface into the bulk of the slag. The rate of reduction of iron and chromium from the slag is greater than the rate of dissolution of the oxides into the slag, i.e. the mechanism of dissolution may change from a first-order process to one of higher order owing to the stirring motion caused by gas evolution during the reduction of the oxides.

In general, the reduction of Transvaal chromite ores occurs via a solid-state reaction with solid reducing agent up to temperatures of about 1500°C. Below that temperature, the presence of SiO₂ increases the rate of reduction of Cr₂O₃ probably by decreasing the free energy of reaction for the reduction of MgCr₂O₄. At slightly higher temperatures, the rates of reaction are increased in the presence of SiO₂, but in this instance because of more rapid dissolution of the chromite ore in a primary slag phase.

It is this capacity of the Transvaal chromite ores, especially in the presence of SiO₂ flux, to reduce relatively rapidly at lower temperatures that is considered to
REFERENCES

15. VAN DER COLF, J. C. G. K. Private Communication.

DISCUSSION

Dr D.D. Slatter*: 

As a result of your work, Dr Urquhart, do you consider that high-carbon ferrochromium (carbon content 4 to 6 per cent) can be produced from a single chromium ore that is difficult to reduce, or should an ore that is difficult to reduce be used in conjunction with a more easily reduced one?

Dr Urquhart: 

Chromite ore that reduces with difficulty is generally included in the mix used for the production of high-carbon ferrochromium with a carbon content of 4 to 6 per cent. This ore in lumpy form tends to form a refining layer at the slag-metal interface and remains in the furnace after tapping. If all the chromite ore fed to the furnace is of the difficult-to-reduce variety, some crushing might be advisable so that the rate of reaction in the furnace can be increased. However, in these times, when good lumpy ore is scarce, this would not be considered in practice.

*Institute of Mining Research, Rhodesia.

205