FACTORS AFFECTING THE REDUCTION RATE OF CHROMITE

N.F. Dawson* and R.I. Edwards[†]

* Council for Mineral Technology
  Private Bag X3015
  Randburg
  2125

† Chemical Engineering Research Group
  Department of Chemical Engineering
  University of Natal
  Durban
  4001

ABSTRACT

Recent laboratory-scale investigations are described, the results of which indicate that a major factor contributing to poor reduction rates (especially of chromium) and extent of reduction is the formation of a very stable magnesio-chromite spinel. Methods are proposed in which disruption of the spinel is induced and the overall reduction process enhanced by the addition of minor quantities of a solvent flux phase. The use of such fluxes enabled an increase of over 20 per cent metallization to be achieved, i.e. in excess of 90 per cent iron and chromium metallization in under. 2 hours at 1300°C, previously achievable only at temperatures of over 1450°C.

Analysis of the test results substantiates the proposed mechanism of reduction in the presence of a solvent flux phase in which, under reducing conditions, all the components of the spinel are sufficiently soluble to enhance pre-reduction of the chromite.

Finally, proposals are put forward on the possible commercial implementation of such a process, which would be of considerable benefit to the ferrochromium industry.

INTRODUCTION

The solid-state reduction of chromite (pre-reduction) prior to submerged-arc smelting is a well-established practice in the production of ferrochromium. In the pre-reduction process, chromite ore and a reductant are finely ground, mixed, and pelletized, and the pellets are then roasted in a rotary kiln at temperatures around 1350°C. The operation has been described in more detail elsewhere[1,2].

A number of advantages have been claimed for the use of pre-reduction prior to smelting, including:

  a reduction in the quantity of high-grade reductant required in the subsequent smelting step,
  the utilization of cheaper and more plentiful chromite fines,
  an increase in chromium recovery in the alloy produced in the smelter, and
  a significant decrease in the electrical-energy requirement of the smelting process.

The saving in electrical energy is of particular importance to the economics of the process. This effect is achieved not only through pre-heating of the ore but, more importantly, through the partial accomplishment of the highly endothermic reduction reaction in the pre-reduction step. The energy requirements for the production of liquid ferrochromium from chromite ore are listed in Table 1.

For reasons given below, the extent of reduction obtained in current pre-reduction practice is seldom more than 60 per cent. This includes almost complete metallization of the iron and hence only a 30 per cent reduction of the chromium oxide to the metal. The reduction in the electrical-energy requirement that can be achieved is therefore limited to less than 50 per cent of the total.

A higher saving in electrical energy is possible only if the degree of reduction of chromium oxide obtained can be substantially increased.

TABLE 1

Energy requirements for the production of
1t of liquid ferrochromium from chromite*

Process step	Energy requirement (kW.h)	Energy requirement (% of total)
Heating of raw materials	1222	39.5
Reduction reactions		
Iron oxides	298	9.6
Cr_2O_3	1157	37.4
Fusion of metal	134	4.3
Fusion of slag	225	7.3
Superheating of metal	23	0.7
Superheating of slag	35	1.1
Total	3094	100

*Assuming a chromite composition of 45 per cent Cr_2O_3, 25 per cent FeO, an efficiency of 100 per cent with alloy and slag tapped at 1700°C and a slag-to-alloy ratio of 1.0

LIMITATIONS OF CURRENT PRE-REDUCTION PRACTICE

The relatively low degree of reduction obtained in current practice is a result of the slow kinetics of reduction of chromite, especially of the Cr_2O_3 content. The kinetics are determined by the temperature of operation, which is limited to a maximum of about 1350°C. This limit is imposed by the properties of the chromite ore and of the fuel ash (if the kiln is fired with pulverized fuel) since, at temperatures

above 1350°C, partial melting of the pellets and the ash occurs, with consequent ring formation in the kiln and hence poor operation.

It will therefore not be possible to achieve higher rates and extents of reduction without substantial changes in current practice.

ENHANCEMENT OF THE EXTENT OF PRE-REDUCTION

Two approaches can be used to overcome the limitation on the extent of reduction outlined above:

(i)   modification of the process to allow operation at higher temperatures (higher than 1500°C) where the kinetics become rapid, or

(ii) improvement of the kinetics of reduction at temperatures compatible with the conventional kiln process.

The first approach has been adopted by Fried. Krupp GmbH[3]. In that process, chromite is reduced at 1550°C in the presence of a siliceous flux and a large excess of reductant. A substantial amount of liquid phase is formed, but it is claimed that the presence of the surplus reductant prevents ring formation. The extent of reduction obtained at that temperature is high and metallizations in excess of 90 per cent are claimed.

A disadvantage of the process is that the surplus reductant must be separated from the slag-metal mixture prior to smelting and, for this to be accomplished, the kiln discharge must be cooled. This results in a substantial loss of the enthalpy of the product, which must be resupplied in the smelter.

The second approach forms the basis of the present study; the factors that limit the extent of reduction at temperatures below 1350°C were identified, and some means by which these limitations can be overcome were devised.

THE KINETICS OF REDUCTION OF CHROMITE IN THE SOLID STATE

The reduction of chromite has been the subject of many previous studies[4-8]; it is a measure of the complexity of the process that, although there is wide agreement on the major features of the reaction, there is no generally accepted explanation of the kinetics.

In general terms, the rate-limiting factor in the reduction reaction can be processes external to the chromite particle (gas diffusion or the rate of the Boudouard reaction) or internal to the particle (gas diffusion through a porous product layer, the rate of the chemical reaction, or solid-state diffusion).

The external factors are amenable to some degree of manipulation and, in this study, the effect of these variables on the rate of reduction was eliminated. However, even when this was done, the rate of reduction remained slow and the reaction incomplete at temperatures below 1350°C. It is therefore reasonable to assume that factors internal to the particles of chromite are rate-limiting in practice as well as in laboratory studies like this one.

The overall rate of reduction of LG-6 chromite was studied by thermogravimetric analysis. Typical reduction curves are shown in Figure 1. However, the data obtained in this way were insufficient for the reduction rates of chromium and iron oxides to be determined separately, so the extents of metallization of iron and chromium were determined as functions of the overall extent of reduction by chemical analysis of the reaction product. Typical metallization curves obtained in this way are shown in Figure 2.

When the above data had been combined, the individual rates of reduction of chromium and iron were separated. Such separate reduction curves are shown in Figure 3. These curves show three features that are of significance in the pre-reduction process: an initial rapid reduction of Fe^{3+} to Fe^{2+} in the spinel lattice, a comparatively rapid and complete reduction of iron oxide, and a delayed and slow reduction of chromium oxide that ceases well before complete metallization is achieved.

In addition to the above analysis of the reduction curves, the reaction products were examined by use of the scanning electron microscope (SEM). The typical appearance of a partially reduced chromite grain is shown in Figure 4, from which it can be seen that metallization occurred exclusively on the surface of the grain. The residual spinel shows no signs of a product layer porous enough to allow significant diffusion of the gases into the interior of the grain. The profiles of iron and chromium concentration across such a grain are typically rather flat.

Analysis of these findings suggests that neither gaseous diffusion through a product layer nor chemical reaction are rate-limiting factors in the reduction of chromite.

The following interpretation is postulated.

(a) The rates of reduction of iron and chromium are determined by the solid-state diffusion of Fe^{2+} and Cr^{3+} respectively through a defective spinel lattice.

(b) The diffusion of Fe^{2+} is comparatively rapid, but is slower than the reduction that takes place at the particle exterior.

(c) As Fe^{2+} is removed from the spinel lattice, a defective structure is created through which Cr^{3+} can migrate, albeit more slowly than Fe^{2+}

(d) As Cr^{3+} is removed from the lattice, a kinetically inert spinel structure, which contains Mg^{2+} in tetrahedral sites and Al^{3+} and Cr^{3+} in octahedral sites, is reformed.

(e) The diffusion of Cr^{3+} ceases for all practical purposes when the ratio of M^{2+} ions to M^{3+} ions in the structure corresponds once again to that of a spinel.

This model of the reduction behaviour of chromite has the following major implications.

The rate and extent of reduction is determined by the chemical composition of the chromite. Therefore the reduction of chromites rich in magnesium and chromium oxides should be more difficult than that of chromites rich in iron and aluminium oxide. This is generally confirmed[6,7].

The rate of reduction of chromite in the solid state can be improved only by the addition of a component that is capable of preventing the formation of kinetically inert chromium-containing spinel. Further studies were therefore undertaken to show whether such a component could be found.

ENHANCEMENT OF REACTION KINETICS

Previous studies[9] have shown that the addition of alkali metal salts such as NaCl leads to improved reduction rates at moderate temperatures. It has been suggested that such agents act by increasing the rate of the Boudouard reaction. At higher temperatures, such reagents should have little effect on the reaction rate, and their use would be problematic because of their volatility and aggressive attack on the furnace refractories.

In the present work, the use of fluorspar (CaF_2), a traditional fluxing agent, was investigated. The results show that a moderate addition of fluorspar does indeed have a beneficial effect on the reduction rate. Further testwork, however, showed that a eutectic mixture of sodium fluoride and calcium fluoride ($NaF-CaF_2$) was very much more effective than fluorspar alone. Further studies were conducted in an attempt to identify the mechanism whereby this eutectic fluoride mixture operates.

Thermogravimetric studies supported by chemical analysis enabled the individual rates of iron and chromium metallization to be determined. Typical results are shown in Figure 5.

A comparison of Figures 5 and 3 shows that the effects of $NaF-CaF_2$ additions on the rates of reduction of iron and chromium are very different. The effect on the rate of reduction of iron is not particularly marked, but that on the rate of chromium reduction is dramatic. The apparent reaction 'ceiling' found previously does not occur in the presence of the fluoride flux addition.

Examination of the reaction product by use of SEM also reveals that it was substantially different from that obtained

in the absence of the fluoride flux. Figure 6 shows a typical chromite grain that was reduced in the presence of the fluoride flux. Four distinct zones can be distinguished: a central core of residual spinel, heavily fractured and with some metallization evident in the fractures, a thin metallized zone surrounding the core, an apparently homogeneous zone, which was found to contain both constituents (Na^+ and Ca^{2+}) of the flux and constituents derived from the chromite (Mg^{2+} and Al^{3+} with very low Cr^{3+} and Fe^{2+}), and an outer metallized zone similar to that obtained in the standard reduction product.

At first sight, these facts are consistent with a mechanism involving the diffusion of Na^+, Ca^{2+}, and F^- into the spinel lattice.

However, a more detailed examination of the apparently homogeneous zone showed it consisted, in fact, of a frozen melt containing almost exclusively the original components of the flux addition, i.e. NaF and CaF_2, in which were imbedded microscopic euhedral crystals of spinel ($MgAl_2O_4$).

Examination of the central, heavily fractured core of residual spinel revealed the presence of only trace amounts of Ca^{2+} or Na^+.

It therefore appears probable that the true mechanism of the fluoride flux is to act as a solvent for the spinel constituents. Fe^{2+} and Cr^{3+} dissolve in the melt together with O^{2-} ions and diffuse to a location where reduction takes place, i.e. at a point of contact between the melt and a particle of reductant. Evidently a small amount of electronic conduction through the melt also takes place, allowing metallization to occur to some extent at the melt-spinel interface.

The non-reducible cations, Mg^{2+} and Al^{3+}, also dissolve in the melt to the limit of their solubility at that temperature, and precipitate as spinel at sites that are energetically favourable.

This model makes it possible to predict the compositions of flux additions that will effectively enhance the reduction rate of chromite. The composition of the flux should be such that:

(1) it has a liquidus temperature below that of the operating temperature,

(2) it is able to dissolve a substantial amount of aluminium and magnesium oxides without a dramatic increase in the solidus temperature, and

(3) the melt formed has a viscosity low enough to permit the rapid diffusion of ions.

Several different flux mixtures, which were considered to be more practical than the original eutectic, were investigated, and it was found that a mixture of alkali feldspar, silica, and fluorspar (2:1:1 on a mass basis) appears to fulfil all the requirements. Such a flux, consisting of finely milled granite and fluorspar, can be conveniently made up and is inexpensive.

Fluxes of this composition were investigated in some detail in laboratory furnaces, the rate of reduction being determined for the temperature range 1100 to 1300°C and for flux additions of between 0 and 20 per cent.

It was found that the resulting rate of reduction is a strong function of temperature and flux addition. At the higher levels of temperature and flux addition, virtually total metallization was obtained in less than 1 hour.

The appearance of the reaction mix changed greatly as the flux addition was increased. At low additions of flux (less than 5 per cent), the liquid phase formed was entirely absorbed into the chromite particles and the charge remained completely dispersed.

At intermediate additions, some sintering of the charge took place but, at a 20 per cent addition of flux and a temperature of 1300°C, extensive sintering occurred. Under the latter conditions, the metal formed mainly away from the chromite surface, and usually surrounded a grain of residual carbon. The non-reducible spinel components also usually recrystallized from the melt, and few residual chromite grains could be identified.

INTERDEPENDENCE OF SPINEL DISSOLUTION AND REDUCTION

In the presence of a flux, at least three separate processes are involved: the dissolution of the spinel constituents, the migration of ions through the liquid phase, and the reaction at the reductant surface. The results obtained from the work reported above cannot be used in a determination of the effect of each of these processes separately on the overall reduction rate. Separate experiments were therefore carried out to show which of these steps was likely to be rate-controlling, since the findings would be of considerable practical as well as academic interest. For example, the pre-reduction step can be followed by a physical separation of the metal formed. For this to be attractive, the degree of metallization should be high and the metal particles as large as possible. The conditions most conducive to the separation process would be the use of a relatively high flux addition and a reductant of coarse particle size, but a high degree of reduction would be obtained only if the rate of diffusion of ions through the melt was not the rate-controlling step.

Attempts were therefore made to estimate the rate of dissolution of chromite in melts with fluxes of the normal composition but with no reductant. These tests resulted in virtually no dissolution of the spinel components in the flux nor in any

recrystallization of new spinels. Instead, it was found that the chromite grains themselves showed extensive recrystallization effects on their surfaces. The original testwork was then repeated with fixed quantities of reductant of different particle sizes, and it was found that the rate of reduction was a strong function of the particle size of the reductant. In experiments conducted with a coarse reductant the rate of reduction decreased considerably. Examination of the reaction product from such tests showed that only those chromite grains near a particle of reductant had undergone major reduction, whereas those further away appeared similar to the ones that had been produced when no reductant was used.

These findings suggest that the reduction reaction and the spinel dissolution process are not independent of each other, and that spinel dissolves only when it is in close proximity to a reductant particle, i.e. when reduction is taking place in its immediate vicinity.

A possible explanation of this is that, in the absence of reductant, the melt immediately adjacent to the chromite particle becomes saturated in one component, probably Cr_2O_3, which then recrystallizes at the surface of the grain,

effectively halting the dissolution process. In some experiments, a separate chromium sesquioxide phase was in fact found close to the chromite surface.

It is therefore concluded that fine grinding of the chromite and reductant and intimate mixing before pelletizing are essential requirements for high degrees of metallization.

POSSIBLE INDUSTRIAL APPLICATION

Several different industrial applications of such flux additions appear possible.

Low additions of flux, i.e. less than 5 per cent, appear to be suitable for use in the pre-reduction process as practised at present. At this level of addition, the liquid phase formed is almost entirely confined to the interior of individual altered chromite grains. The behaviour of the pellets at temperature in the kiln should therefore not be greatly affected.

At this level of addition, the rate of reduction should increase sufficiently to produce a highly metallized product in the residence time (more than 4 hours) currently used.

Partial re-oxidation of the pellets prior to smelting (to increase their electrical resistance) would be necessary, but this is normally done in any case.

Although some fluoride and alkali would be introduced into the smelter slag, these would be present at such low levels (less than 1 per cent each) that no major problems should be encountered.

An increase in chromium metallization from the usual 30 per cent to 80 per cent would appear attainable. This would result in a decrease in the consumption of electrical energy in the smelter of approximately 600 kW.h per ton of metal produced.

Higher levels of flux addition would not reduce the consumption of electricity much further. The extra cost of, say a 20 per cent flux addition could not be justified on this basis alone.

However, this additional cost could be

justified if the increase in the rate of reduction were sufficient to significantly decrease the time required for complete reduction of the chromite, because a smaller pre-reduction kiln would be required, which would involve less capital expenditure.

A sufficient increase in reduction rate was demonstrated in the laboratory. However, on an industrial plant, other factors may become rate-limiting; in particular, the rate of heat transfer to the pellet is likely to limit the rate of reduction, especially if a rotary kiln is used.

This suggests that large additions of flux will necessitate the use of equipment with good heat-transfer characteristics, and shaft kilns are the obvious choice. Such kilns are, however, very susceptible to sintering of the charge and, at high flux levels, this could present serious difficulties. The annular kiln developed by the Associated Portland Cement Manufacturers Limited[10], and already in use in the ferrochromium industry, could prove to be the most appropriate device for use in this application.

Flux additions at the 20 per cent level may also necessitate some changes in smelter operation. The level of fluoride in the slag will rise to around 3 per cent and, at that level, will have a pronounced effect on the properties of the slag. It would also be necessary to determine the effects of a high degree of pre-reduction and changes in the composition of the smelter slag on the level of impurities in the metal produced.

Although these results have been obtained only on the laboratory scale as yet, the potential for industrial application appears to be substantial. Further trials on a larger scale are envisaged.

ACKNOWLEDGEMENTS

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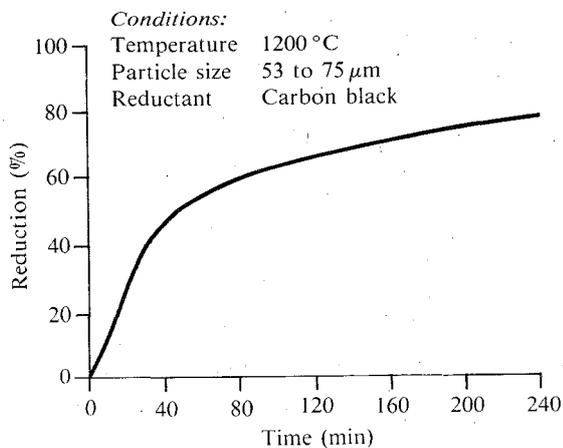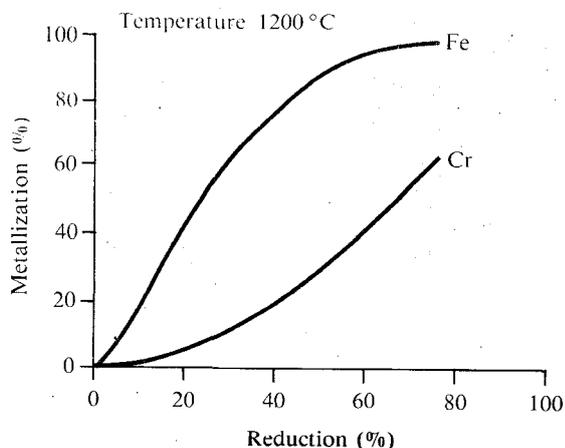
Fig. 1. Rate of reduction of LG-6 chromite

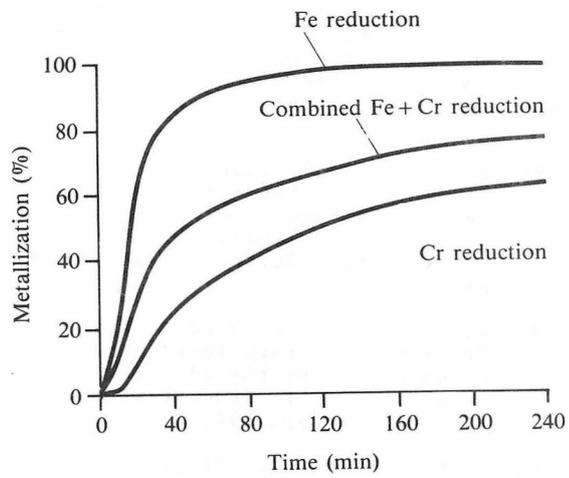Fig. 2. Individual metallization of iron and chromium during the reduction of LG-6 chromite

Fig. 3. Chromite reduction in terms of the individual rates of metallization of iron and chromium
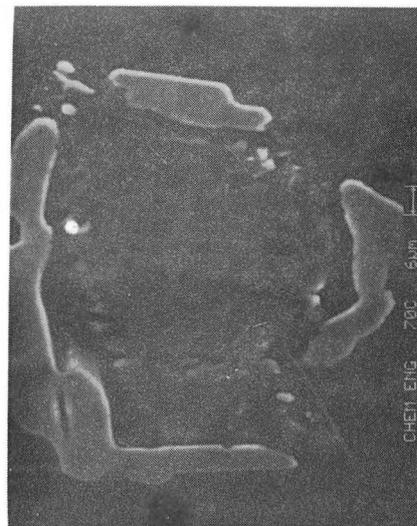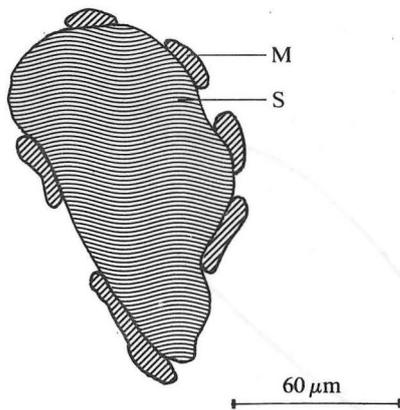

Fig. 4. Typical appearance of a grain of chromite after partial (70 per cent) reduction at 1200 °C.
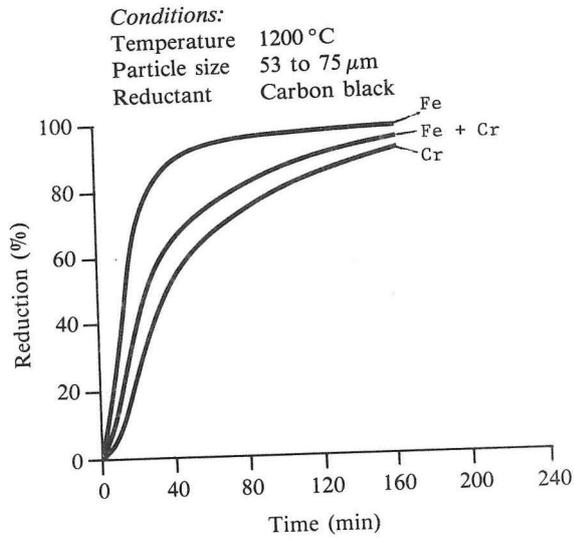M = metal; S = spinel

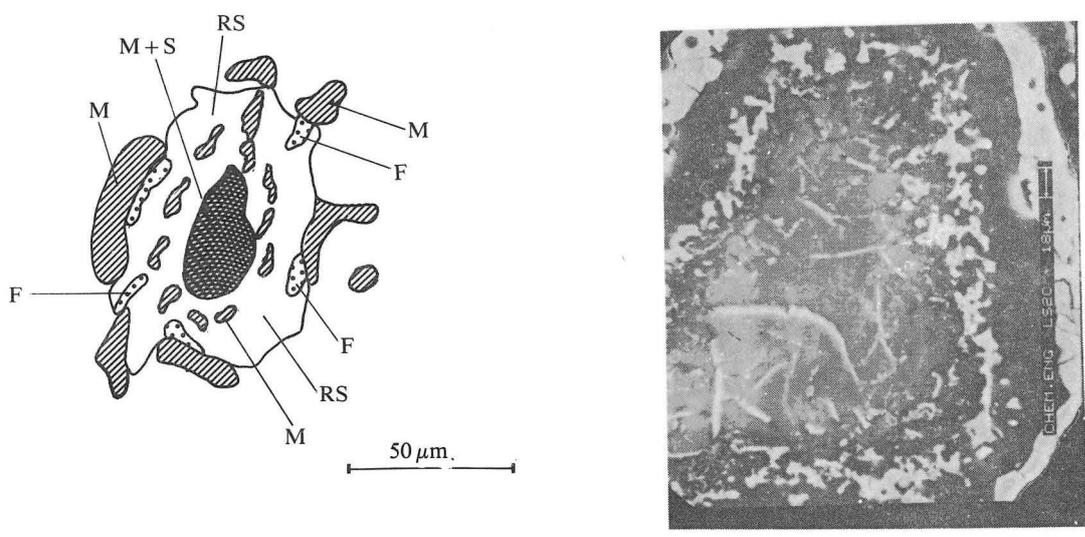Fig. 5. Reduction of chromite ore with a 10 per cent fluxing addition of NaF–CaF₂

Fig. 6. Typical appearance of a chromite grain after reduction in the presence of a low-temperature flux phase. M = metal; S = spinel; RS = recrystallized spinel; F = flux