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INDURATION OF CHROMITE

LJ Erasmus
GENCOR Process Research, South Africa

ABSTRACT

Pre-oxidation of chromite pellets has been claimed to improve the electrical efficiency and thus productivity of ferrochrome production. A laboratory investigation was undertaken in search of the fundamental reasons for claimed improved productivity when using indurated/pre-oxidised chromite pellets.

The experiments were aimed at determining whether prior oxidising heat treatment might influence the behaviour of the chromite during subsequent reduction - in terms of the kinetics at a particular temperature or the temperature where active reduction sets in.

It was concluded that pre-oxidised chromite in the furnace feed should improve the productivity of a cold charged furnace. The carbon consumption in the furnace should not increase significantly, if at all. Preheating of the charge, or part of it, will enhance the effect of improved reducibility. Replacement of lumpy ore by high quality indurated pellets should also result in energy savings.

INTRODUCTION

An experimental programme was undertaken to evaluate the effects of simple preheating under oxidising conditions on the reducibility of different South African chromites.

Prior oxidation is unlikely to influence the reaction energy demand in a ferrochromium furnace significantly. Energy saving may be expected to result through fruitful utilisation of energy that is presently being wasted, because it is only available at low temperature. For this reason the experimental programme focused on conditions that must be classified as 'mild' for chromite reduction. In the light of this and in order to limit the amount of experimental work, the programme was more specifically constrained as follows:

(a) Rate of reduction measurement, routinely with carbon as reducing agent, at temperatures not exceeding 1300°C, using comparatively large chromite particles.
(b) A narrow chromite size particle size range to largely eliminate size as a kinetic variable.
(c) As complete removal of extraneous gangue as can be achieved by physical (gravity) means and avoiding flux additions - as such or in the form of binders for agglomeration. Certain fluxes are well known to act as 'promotors' in chromite reduction.
(d) Carbon monoxide instead of carbon as only reductant.

EXPERIMENTAL WORK

Chromite sample preparation and designation

Altogether five samples were investigated. The choice was not based on mineralogical differences but with the aim of covering both chromites presently charged to ferrochromium furnaces and those that are not yet exploited for their chromium content. The various samples are listed in Table 1.

TABLE 1 : Chromite concentrate samples

Sample	Chromite concentrates
LG6FR	LG-6, Fraible, gravity concentrate
LG6LU	LG-6, Lumpy, HMS concentrate
UG2A	UG-2, Gravity concentrate
UG2B	UG-2, Gravity concentrate, but with smaller grain size and less friable
MG2	MG-2, Gravity concentrate

The samples were reduced to -300 μm before being cleaned on a laboratory shaking table with the aim of removing as much as possible of the extraneous gangue. The oxidation and reduction tests were performed on particles in the root-two size range -212 +150 μm. This particular fraction was dried at 100°C for 48 hours and submitted for iron and chromium analysis.

THE THERMOGRAVIMETRIC EQUIPMENT

A vertical tube furnace, fitted with silicon carbide elements, was used. The inside diameter of the recrystallised alumina worktube is 65 mm and the cylindrical crucibles of the same material that held the reacting samples, had an inside diameter and height of 45 mm and 75 mm respectively. The crucible stood on a mullite pedestal, supported by an alumina tube (thermocouple protection sheath) which was clamped to the modified pan of a top-loading electronic balance. The latter stood on the platform of a motorised lift. With the crucible in position in the hot zone, the balance-worktube assembly formed a gas tight system with provision for controllable gas through-flow from gas cylinders and temperature measurement at the level of the crucible rim. A computerised data-logging system was used to record time, temperature and sample mass during experiments.

Pre-oxidation

The aim was to effect as near as possible complete oxidation of the ferrous oxide component of the spinel to Fe_2O_3. In order to define the necessary conditions for routine achievement of this aim, preliminary thermogravimetric work was done on 100g chromite samples. The temperature programme used involved a constant-rate increase from ambient to 1100°C over 7 hours, followed by 4 hours at 1100°C. Air was passed through the furnace worktube at constant flowrate during the entire experiment. From this work it was concluded that oxidation in air at 1100°C for 4 hours would be adequate to achieve nearly complete oxidation, and this set of conditions was therefore subsequently used to prepare oxidised chromite samples in an ordinary muffle furnace. Even so the overall mass gain in the preparation was always determined and compared with the maximum possible gain.

Reduction

Finely powdered lampblack was used as reducing agent in all the experiments but one. It was mixed intimately with the 50g chromite charge and the mixture was contained in the alumina

reaction crucible. In most experiments the carbon addition was based on the requirement for reducing the iron oxides to iron and Cr_2O_3 to chromium, which is defined as the 'stoichiometric carbon requirement'. Allowance was in most experiments made, in terms of extra carbon, for the removal of the extra oxygen that had reacted with the chromite during pre-oxidation.

Most of the reduction experiments were conducted under rising temperature conditions for more time-effective detection of behavioural differences among the chromites and between a chromite and its pre-oxidised form. The temperature was raised at a constant rate from 600° to 1200°C over 4 hours, while the sample mass was monitored continuously. An inert (argon) atmosphere was maintained over the sample during this recording period.

Several experiments were conducted isothermally at 1200° or 1300°C. Apart from the constant temperature the basic procedure was the same as that described above.

In either case the temperature of the furnace was first raised and allowed to stabilise at the desired value, with the loaded crucible positioned on its pedestal just below the (open) worktube. Flushing with argon then started and the crucible was raised to a position about 250 mm below its final position in the hot zone to allow closure of the balance box-worktube coupling. The crucible was then raised to its final position in one minute and mass recording commenced. The entire insertion procedure took 5 minutes. The argon flow through the worktube was maintained constant at 1230 ml/min. On completion of an experiment the sample was allowed to cool under argon to a temperature below 500°C, in order to ensure that the final degree of reduction was unaltered. A few of these final products were subjected to mineralogical investigation.

RESULTS AND DISCUSSION

The characterisation of these five chromites are shown in Tables 2 and 3. Detailed results for LG6FR and UG2A are shown in the figures. The behaviour of the other three does not differ markedly from that of LG6FR and UG2A.

Preliminary characterisation of the chromite concentrates

Chemical analyses

The samples were only analysed for chromium and iron and the results are given in Table 2.

TABLE 2 : Chromium and iron contents of the various concentrates

Chromite	Cr_2O_3, %	Fe, %	Cr/Fe
LG6FR	46.1	20.4	1.549
LG6LU	46.2	21.0	1.509
UG2A	44.1	22.9	1.317
UG2B	43.5	21.8	1.370
MG2	43.8	21.7	1.382

Iron oxidation state and stoichiometric carbon requirement

The spinel can generally be represented by $X^{2+}Y_2^{3+}O_4$ where X is mainly Fe, Mg or Mn and Y is Cr, Al or Fe. Iron therefore occurs in both the tetrahedral and octahedral lattice sites. Metallurgically the Fe^{3+}/Fe^{2+} ratio is obviously important because it determines the amount of oxygen to be removed in reduction and therefore the stoichiometric amount of reductant required for complete reduction. The Fe^{3+}/Fe^{2+} ratio was determined thermogravimetrically by oxidising the chromite to constant mass in a rising temperature-constant temperature (1100°C)

experiment. The results of two such experiments are shown in Figure 1. The degree of oxidation was obtained by taking the final (maximum) mass increase as corresponding to full (100%) oxidation of Fe^{2+} to Fe^{3+}. This also allows the Fe^{2+} and Fe^{3+} contents of the chromites to be calculated - as shown in Table 3.

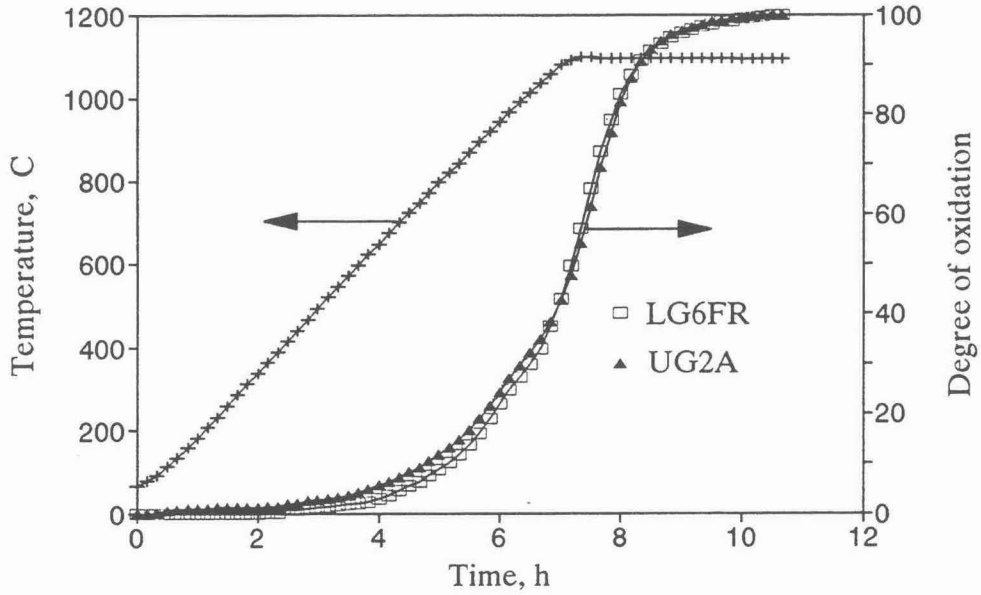


FIG.1. Results of oxidation experiments on chromites LG6FR and UG2A

TABLE 3 : Calculated concentrations of the iron oxides in the various concentrates

Chromite	Fe_2O_3, %	FeO, %	Fe^{3+}/Fe^{2+}
LG6FR	8.666	18.403	0.424
LG6LU	10.290	17.740	0.522
UG2A	10.720	19.857	0.486
UG2B	7.686	21.084	0.328
MG2	9.845	19.041	0.465

These figures are considered adequately reliable. The Fe^{3+}/Fe^{2+} ratio for the LG6FR and UG2A concentrates could be compared with actually analysed values[1] and were found to differ from these by a maximum of 0.003.

From the analyses in Table 3 the total removable oxygen and stoichiometric carbon addition for reduction of the iron oxides to iron and chromium oxide to chromium could be calculated for the unoxidised chromites.

Calculation of degree of reduction

Reduction of the original/unoxidised chromites with carbon

The percentage reduction was calculated per unit mass unoxidised chromite as:

$$\text{(Actual mass loss) / (Maximum mass loss) x 100} \qquad (1)$$

The denominator was calculated for the removable oxygen, either from ($FeO+Fe_2O_3$) in which case the degree of reduction was referred to as 'Iron reduction' or from the total removable oxygen, including that associated with Cr_2O_3 to give the 'Total reduction'.

Reduction of pre-oxidised chromites with carbon

In order to facilitate comparison with the figures for reduction of the unoxidised samples, the denominator was the same as in (1), but the numerator was changed to:

(Actual mass loss)-(mass gain during oxidation) x 28/16 (2)

This means that the degree of reduction was negative until oxygen that had been added during pre-oxidation was removed. Thereafter the reduction for oxidised and unoxidised samples are directly comparable.

Reduction with carbon: Rising temperature

The constant rate of increasing the temperature (about 2.5°C/min.) was slow enough to indicate 'a minimum temperature for kinetically significant reaction', to be used later in the isothermal experiments, but also to compare the various chromites directly.

Reduction of unoxidised chromites

The results are shown in Figure 2. In general, the measurable reduction begins between 1000° and 1100°C, but up to 1200°C the actual degree of reduction attained is small.

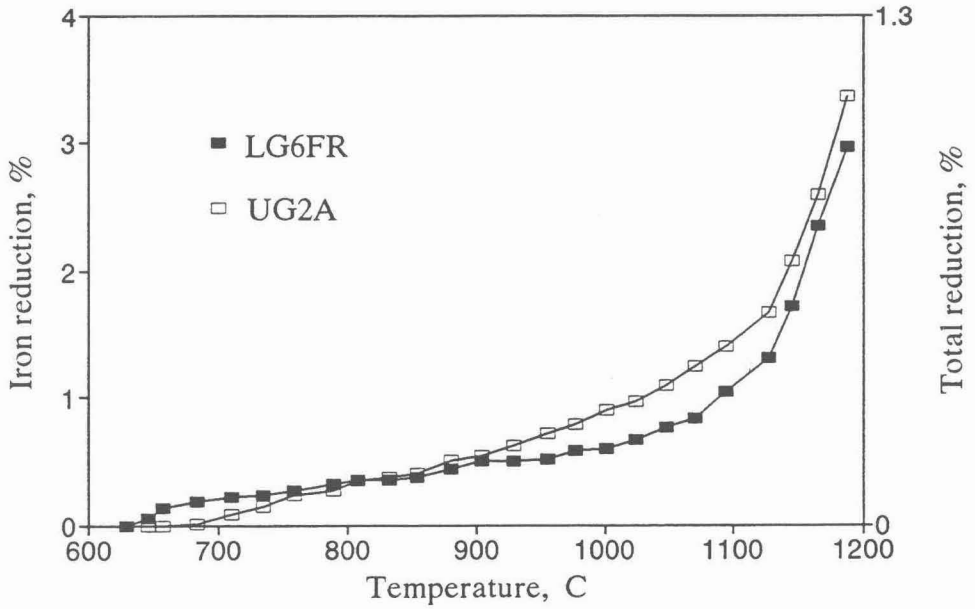


FIG.2. Reduction of unoxidised chromites with carbon (rising temperature)

Reduction of pre-oxidised chromites

All the chromites were subjected to the same treatment and the results are summarised in Figure 3. The chromites clearly behaved very similarly over the temperature range that was covered. Active removal of the equivalent oxygen that was picked up during prior oxidation starts at about 950°C and this phase is completed at between 1020 and 1040°C. The rate then decreases slightly, only to start increasing again at around 1150°C, to attain iron reduction of approximately 30% at 1200°C (to be compared with approximately 3% for unoxidised chromites).

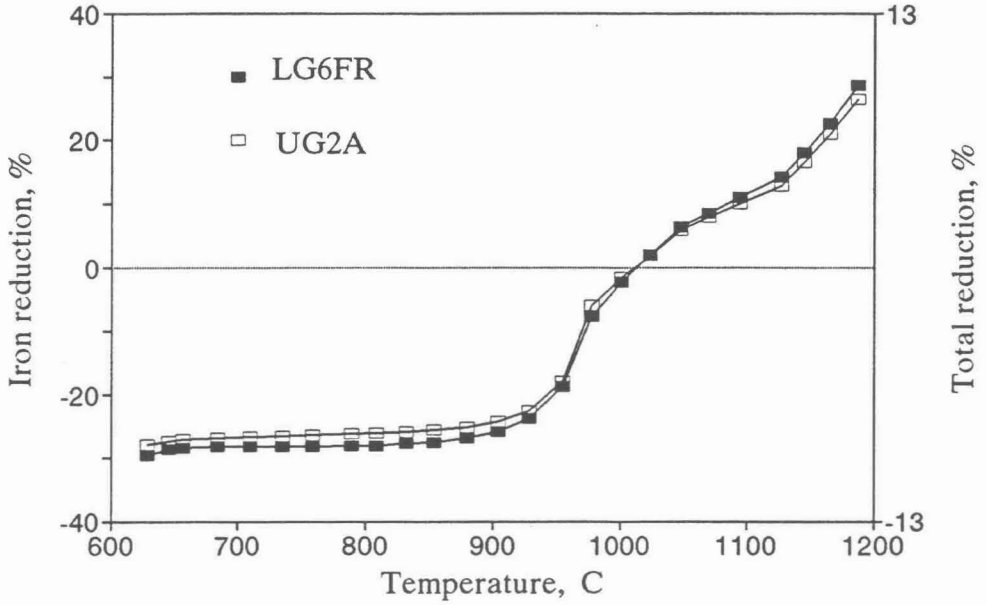


FIG.3. Reduction of pre-oxidised chromites with carbon (rising temperature)

One explanation is that the initial reaction is metallic iron formation by reaction between the newly formed, readily accessible Fe_2O_3 and CO, although some starting C-O reaction would be required, forming some CO_2. However, at 950°C the Boudouard reaction becomes sufficiently active to ensure a high p_{CO}.

The reaction then slows down briefly due to metallic iron presumably limiting access of CO to the remaining iron-deficient spinel. The final increase in the rate is thought to be due to reduction via Fe_3C (diffusion of carbon through a metallic product layer) becoming effective.

It should be emphasised here that the 1200°C degree of reduction attained is by no means 'advanced' in terms of the total removable oxygen - total reduction only being around 10%. The most important reason is that very little chromium is metallised - Cr_2O_3 remains very stable, whether it is now partially available as a separate phase or as a mixed gamma phase (M_2O_3) or not. Also 1200°C is low for normal chromite reduction, as was illustrated for the unoxidised chromites. Finally the particle used in these experiments (-212 +150 μm) is coarse in comparison with what has come to be acceptable as desirable for pelletisation (around 75% -75 μm).

Reduction with carbon monoxide: Rising temperature

Even though the equivalent amount of oxygen gained during pre-oxidation is very readily removable, extra oxygen in the furnace burden requires extra reductant. It was therefore important to determine whether the additional oxygen would react with carbon monoxide, as the

rising furnace gas is rich in CO. Only a single experiment was performed - on the LG6FR concentrate. The rising temperature regime was as before up to 1200°C. The flow rate of CO through the furnace was maintained at 1 *l*/min.

The results are compared in Figure 4 with the corresponding experiment with carbon as reductant. Active removal of oxygen starts early at around 700°C, compared with 950°C in the case of carbon. This phase is also completed earlier (950°C compared with 1000°C). This behaviour is explained by the independence of the reduction mechanism of the Boudouard reaction when carbon monoxide is used.

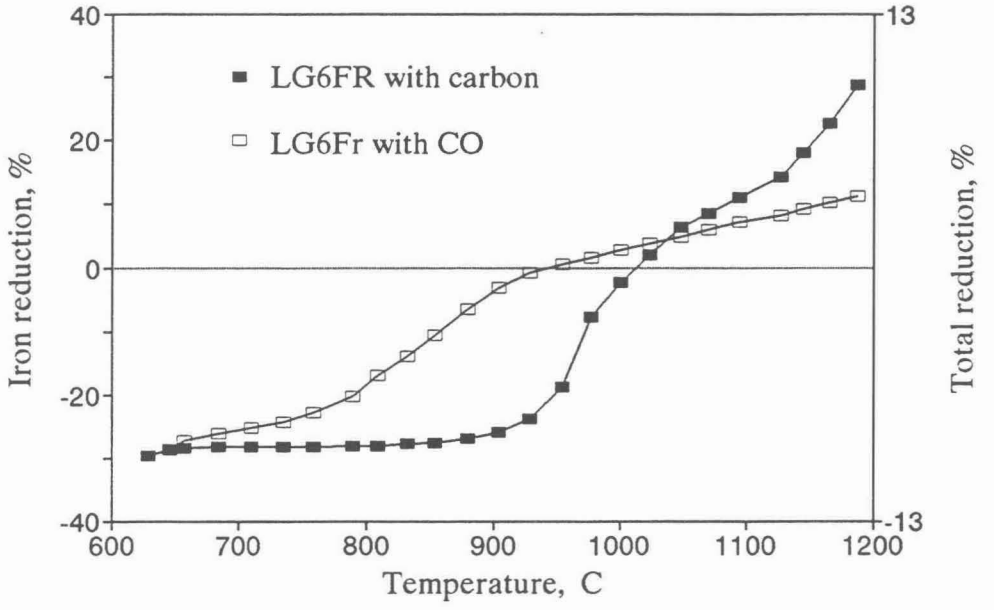


FIG. 4. Reduction of pre-oxidised LG6FR with carbon and CO as reductant

Again the reaction slows down after removal of the 'readily accessible' oxygen, but this time the rate does not increase markedly again around 1150°C as it did with carbon. This is presumably due mainly to the lack of carbon able to dissolve in the metal phase and to be transported to the reaction interface.

Even so, the ultimate degree of reduction was considerably higher than that attained with carbonatious reduction of the unoxidised chromite. Furthermore, the early start of reduction with CO definitely adds motivation for charging pellets that had been indurated under oxidising conditions to the furnace. It implies that an equivalent amount of the oxygen added during prior oxidation can be removed with 'waste CO' and that the carbon consumption in the furnace is unlikely to be increased by prior oxidation, while the faster rate advantage of prior oxidation is retained.

Reduction with carbon at constant temperature

Because of the similarity in reduction behaviour of the various chromites that had emerged from the rising temperature test series, constant temperature work was limited to LG6FR and UG2A.

Reduction at 1200°C with stoichiometric carbon

The results are summarised in Figure 5. Again the two chromites reacted very similarly, and the effect of pre-oxidation was quite remarkable, with iron reduction values of around 55% being

attained after 3 hours, compared with less than 20% for unoxidised samples. Attention is drawn to the fact that the total reduction was low at around 5% after 3 hours for the unoxidised samples and less than 20% for the oxidised ones. This is due to the large particle size. For example, Barnes[1] recorded total reduction values of 55 to 70% for similar chromites of which the bulk of the mass was smaller than 75 μm.

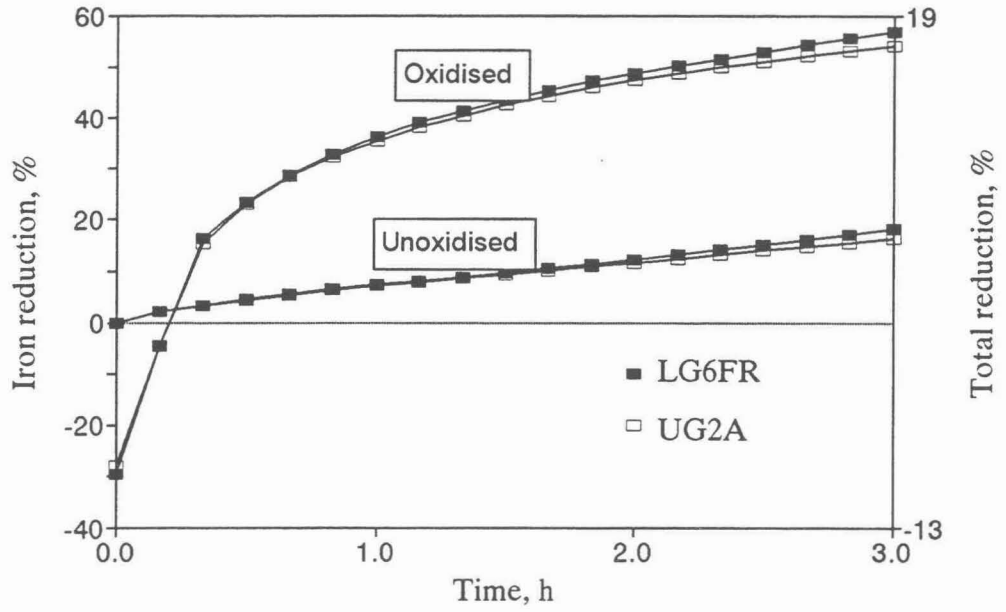


FIG. 5. Reduction of LG6FR and UG2A at 1200°C with stoichiometric carbon

The effect of temperature on the rate of reduction with stoichiometric carbon

Figure 6 shows reduction against time curves for both oxidised and unoxidised LG6FR at temperatures of 1200 and 1300°C. Iron reduction values in excess of 100% do not imply 100% iron metallisation with some chromium metallisation beyond that only, although it is true that some 80% of the iron can be metallised before significant chromium metallisation starts. The metal phase in the products of 1200°-reduction also contained some chromium - more in the pre-oxidised sample, as will be shown later.

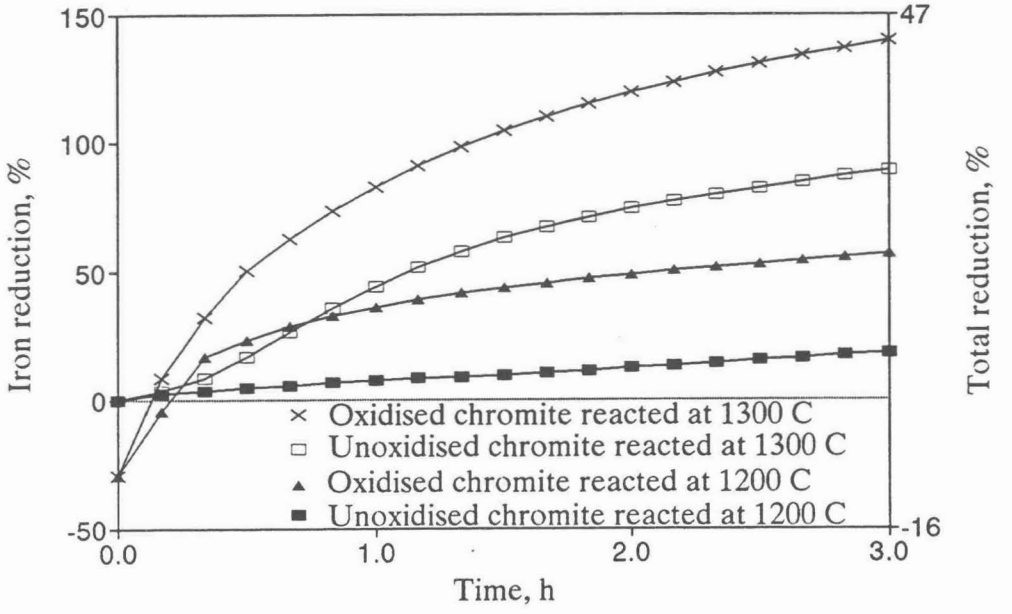


FIG. 6. The effect of temperature on the rate of reduction of LG6FR

Probably the most remarkable feature of the 1300°-curve for the pre-oxidised chromite is that, although the rate slows down somewhat to a virtually constant value beyond an iron reduction value of 120%, it is still relatively fast over the interval 80% to 120% where chromium reduction undoubtedly occurs. This does seem to confirm the existence of also a more readily reducible form of chromium oxide, whereas in the case of the unoxidised sample chromium oxide reduction may be retarded by protecting $MgO.Al_2O_3$ (on removal of FeO and Cr_2O_3).

The effect of carbon addition rate

As explained in par 2.4, allowance was made in the reduction runs on pre-oxidised chromites for the fact that these samples had more removable oxygen per unit mass than their unoxidised counterparts, by addition of extra carbon to maintain a stoichiometric supply for reduction of iron oxides to iron and Cr_2O_3 to chromium. In a single experiment of LG6FR the effect was investigated of not making this allowance. It is to be anticipated that the ultimate metal recovery will be low in this case and that the reduction reaction will slow down towards the end, but the experiment was performed to assess the effect during the early parts, where the carbon may still be considered to be in excess to what is required for iron reduction only. The results are shown in Figure 7. It is clear that the reduced carbon addition did affect the rate of reduction of the pre-oxidised sample adversely. However, the initial rate is still very significantly faster than that of reduction of the unoxidised chromite with its stoichiometric carbon addition.

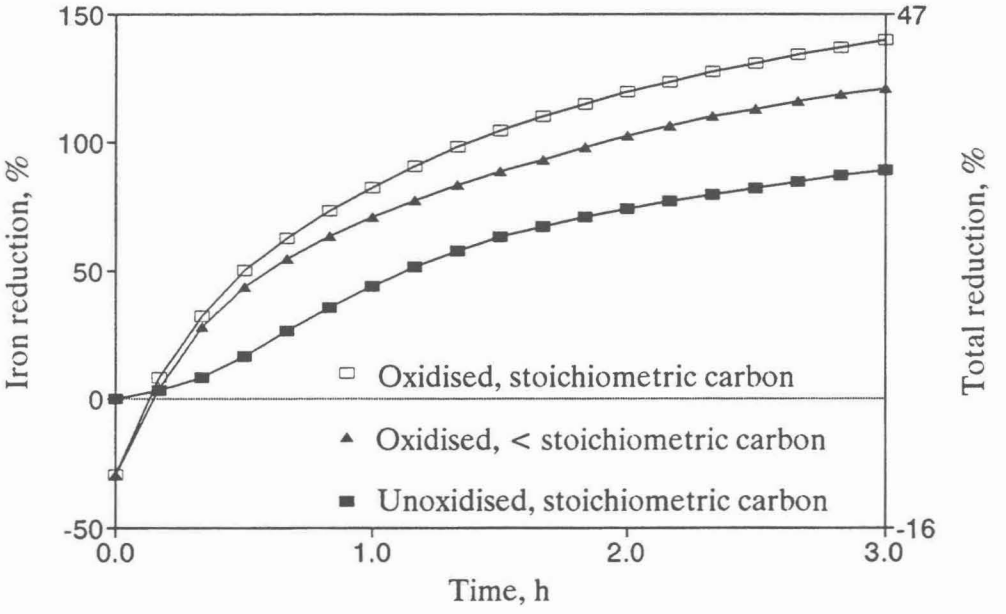


FIG. 7. The effect of carbon addition rate on reduction of LG6FR at 1300°C

Mineralogical investigation

A summary of the important mineralogical findings for a suite of LG6FR samples is discussed next. The samples investigated are shown in Table 4.

TABLE 4 : Description of samples

Figure	Sample history
8	Chromite, as received
9	Chromite after pre-oxidation at 1100°C for 4 hours
10	As received chromite, reduced with carbon at 1200°C for 3 hours.
11	Pre-oxidised chromite reduced with carbon at 1200°C for 3 hours.

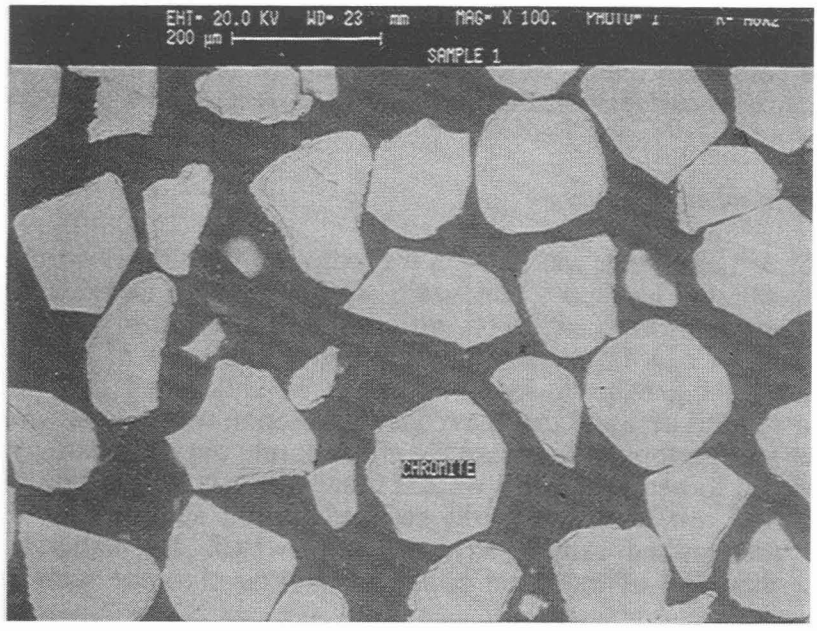


FIG. 8. Chromite as received

The effect of pre-oxidation (Figure 9)

(a) The original spinel has been severely altered - only Phase II resembles it, and even this is not a perfect spinel, being enriched in MgO (relative to FeO) and being heavily contaminated with gamma (M_2O_3) phase (compare with Figure 8).

(b) Part of the iron does report at the grain boundary as virtually pure iron oxide (Phase III), and the rest forms part of the 'exolved' gamma-phase (Phase I), which also contains part of the Cr^{3+} and Al^{3+}.

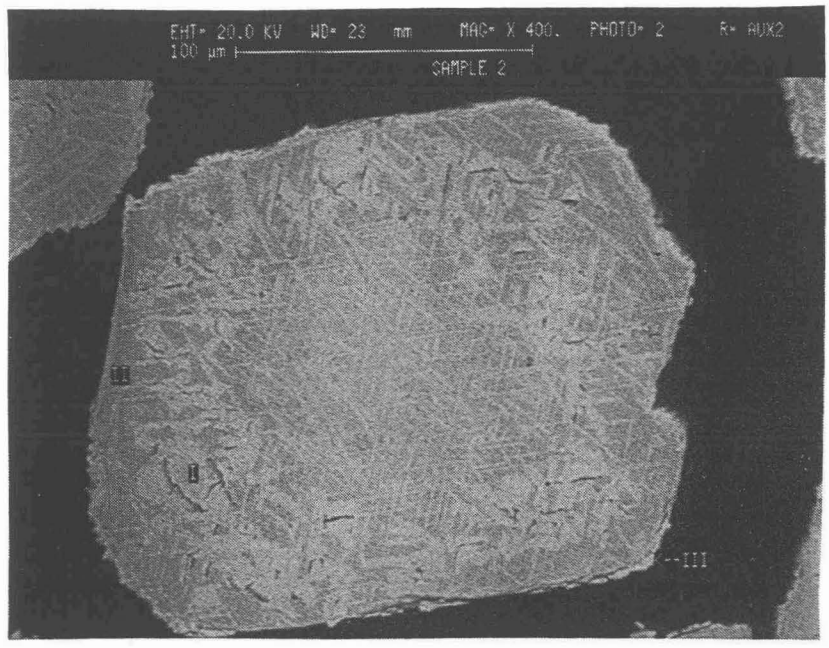
Under reducing conditions the surface oxide should react very readily. It may also be expected that the iron oxide component of the gamma-phase will react more readily than that in the original spinel. Another important advantage of pre-oxidation probably lies in the fact that the gamma-phase grows out of the host, creating new stressed interfaces and fractures that may allow improved access of the reductant, apart from the fact that the particle size of the solid reactant is effectively reduced.

(c) There is probably more chromium remaining in the host spinel than reporting in the gamma-phase so that, at first sight, Cr_2O_3 reduction will probably not be much improved. However, the early formation of the iron metallic phase - now at many more points of contact with the spinel - could in fact also promote chromium metallisation substantially.

Reduction of unoxidised chromite (Figure 10)

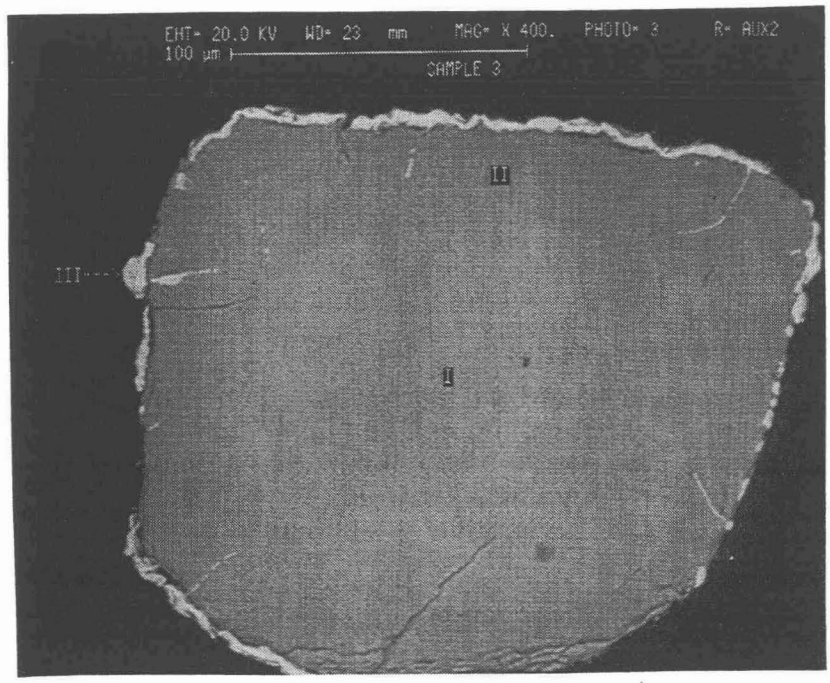
Metallisation is almost entirely limited to the grain boundaries. In its effect on the host mineral, the removal of iron to the grain boundary (to be metallised there in this case) is rather similar to what occurs during prior oxidation, ie. the formation of gamma-rich spinel. But in this case, with a core of original spinel still remaining, the gamma-rich spinel does not disproportionate to precipitate the gamma-phase. Instead, it will remain as an intermediate through which iron has to diffuse from the original spinel core, until the latter is exhausted.

After this chromium oxide reduction will start from the altered spinel, leaving again ordinary spinel ($MgO.Al_2O_3$) as a protecting layer between the metal and the altered spinel core. Reduction of chromium from the pre-oxidised sample will be similarly retarded, but much less so, because of the immediate proximity of metal bleps formed from precipitated gamma-phase.



Exsolution lamellae (I) of Fe^{3+}-rich Cr-Al oxide in host (II) of Fe^{2+}-rich Cr-Al oxide. Phase III is a rim of Fe^{2+} oxide (wuestite or goethite).

FIG. 9. Chromite after pre-oxidation at 1100°C for 4 hours.

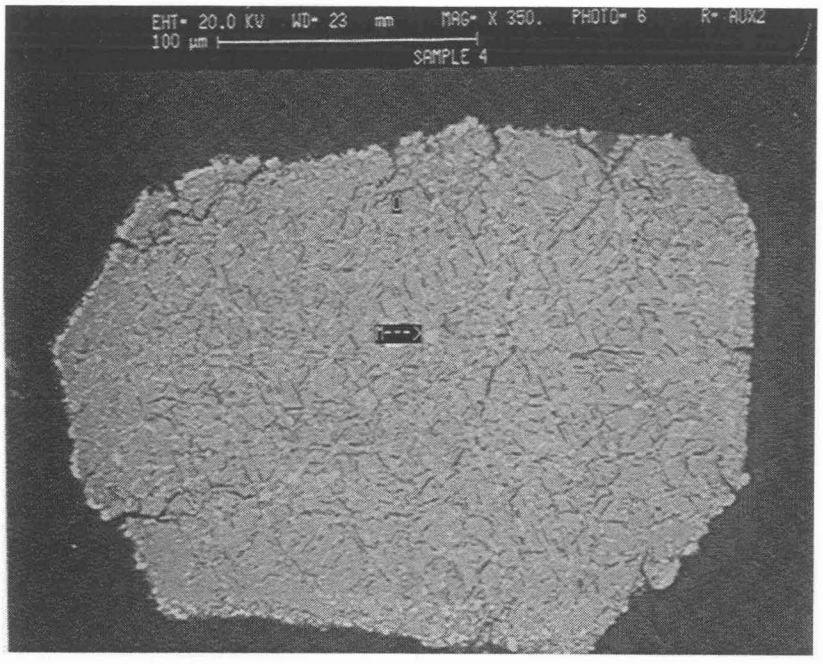


Metal phase (III) developed on the borders of spinel-like phases I and II

FIG. 10. As received chromite, reduced with C at 1200°C for 3 hours.

Reduction of pre-oxidised chromite (Figure 11)

The dispersed metallisation and the nature of the phases that were observed in this instance, are generally in accordance with the earlier expectations, formulated in par. 3.6.2, on the basis of the nature of the pre-oxidised sample.



Metal phase (M) occurring in cracks, cleavage directions and grain boundaries of oxide phase (O).

FIG. 11. Pre-oxidised chromite reduced with C at 1200°C for 3 hours.

CONCLUSIONS

A variety of gravity cleaned South African chromites were tested for their reducibility with carbon and carbon monoxide in the solid state, with and without prior oxidation, and the following conclusions may be drawn from the experimental observations:

(a) The chromites differ very little in their reducing behaviour, but those with high FeO content in the spinel (UG2A and UG2B) do tend to reduce slightly faster, particularly when not oxidised beforehand.

(b) Prior oxidation has definite beneficial effects on the kinetics and extent of subsequent reduction. An equivalent amount of the oxygen picked up during the oxidation is rapidly removed during reduction at a temperature considerably lower than that at which normal chromite reduction starts. This has the effect of early metal phase formation, which again promotes further reduction of first iron and eventually chromium. Mechanistically this is due to the formation (during oxidation) of virtually pure iron oxide at the grain boundaries as well as the disproportionation of the remaining spinel into an altered spinel host and a gamma-phase, so increasing the reaction interfacial area dramatically.

(c) Pre-oxidised chromite requires more reducing agent for total reduction in a submerged-arc furnace, but at least up to the point of complete iron metallisation reduction of the pre-oxidised chromite remains much faster than that of the unoxidised chromite with the same amount of carbon, although it is somewhat slower than what it could be if allowance is made (in terms of extra carbon) for the removal of the extra oxygen.

(d) The removal of extra oxygen from pre-oxidised chromite can also be effected with CO as reducing agent. In fact this reaction starts at an even lower temperature than the corresponding one with carbon. Moreover, this reaction is slightly exothermic at the temperatures of interest.

REFERENCE

1. Barnes, A.R., and Finn, C.W.P. NIM Report No 2070, 30 October 1980.