PRE-REDUCTION OF FLUXED CHROMITE-ORE PELLETS UNDER OXIDIZING CONDITIONS

Robert C. Nunnington
and
Nicholas A. Barcza

Council for Mineral Technology
(Mintek), Randburg, Republic of
South Africa

INTRODUCTION

The production of ferrochromium by the conventional submerged-arc route has, in recent years, faced increasingly serious competition from alternative process options. These include electrically based operations using the open-bath d.c. transferred plasma-arc furnace[1] and the shaft furnace based on non-transferred-arc heaters[2], and fossil-fuel-based processes either for pre-heating and/or prereduction prior to smelting, or for the production of materials that are used directly in the manufacture of stainless steel[3,4]. The new processes are aimed at the lowering of variable costs by the utilization of cheaper ore and reducing-agent fines, and by minimization of the energy costs. Energy based on coal combustion is considerably less expensive than electrical energy, provided that thermally efficient utilization can be achieved at a reasonable capital cost.

In South Africa, which has a fairly high inflation rate recent developments indicate that increasing interest is being shown in the installation of processes that are more capital-intensive and are likely to incur significantly lower variable costs[5]. So far the only commercial operation that has been used successfully for the pre-reduction of chromite is the rotary-kiln process which involves the treatment of composite pellets[6]. However, the capital costs of the rotary kilns and smelting furnaces required are high compared with those of submerged-arc furnaces of equivalent production ratings. There are therefore strong incentives to improve the output of existing rotary kilns and, hence, the cost-effectiveness of the process. It has been reported that the rate and extent of pre-reduction can be enhanced by the use of fluxes[7]. However, although there is considerable scope for improvement, the rotary-kiln process has certain apparent constraints with regard to the achievement of a rapid heat-transfer rate and high thermal efficiency. Interest in the rotary-hearth furnace for the pre-reduction of chromite has increased since it appears to offer some advantages over the rotary kiln[8].

The attainable efficiency of combustion of a fuel, e.g. pulverized coal (PF) or carbon monoxide gas, is directly related to the extent of its combustion to carbon dioxide but the overall efficiency of the process depends on the manner in which the heat transfer is effected. Chromite ore cannot be pre-reduced effectively when the heating gas that is in close contact with the mixture of chromite and carbonaceous reducing agent contains even a small amount of carbon dioxide, or if the exit temperature of the combusted gas is high. In the shaft furnace, which is less costly than the rotary kiln or the rotary-hearth furnace, the heating gas is in close contact with the charge, and this precludes its use for the pre-reduction of chromite-ore pellets.

The Council for Mineral Technology (Mintek) initiated a research programme in an effort to develop technology that would maximize the rate and degree of reduction of chromium and iron, as well as the overall energy-efficiency of the process. Laboratory- and small-scale pilot-plant tests successfully demonstrated that the use of a thin coating of ferrochromium or aluminosilicate on the surface of composite chromite pellets permits the reduction of over 70 per cent of the chromium oxide and 90 per cent of the iron oxide under atmospheres containing 100 per cent carbon dioxide. This development follows the use of fluxes to enhance pre-reduction, and has paved the way for a serious consideration of the use of shaft furnaces into which carbon monoxide gas from (for example) a smelter-gasifier could be passed. This would effect high levels of pre-reduction of coated chromite pellets containing limited amounts of flux to enhance pre-reduction. Hitherto an alternative use for the surplus gas from such a smelter-gasifier had to be considered[9].

EXPERIMENTAL APPROACH

In previous work at Mintek[7], thermogravimetric analysis (TGA) was used as a technique for the determination of the isothermal reduction rate of fluxed composite chromite pellets at between 1200 and 1400°C. The levels of reduction and metallization attainable were evaluated as a function of time by use of these TGA data and the results of tests in which the pre-reduced pellets were leached with acid so that the soluble (i.e. metallized) chromium and iron species could be quantified.

A similar approach was adopted in the present work but, because it was difficult to interpret the TGA results, only the percentage metallization of the chromium and iron in the pellets was determined. The difficulty arose because the carbon dioxide in the gas phase and the carbon in the pellets caused carbon monoxide to be generated by the Boudouard reaction. The approach involved leaching of the pre- reduced pellets with hydrochloric acid at 95°C. (Details of the leaching method and the metallization formulae are given in Appendix A.)

Apparatus

All the TGA runs were carried out at 1300°C on a standard TGA apparatus built at Mintek, which utilizes on-line data-logging facilities to record sample mass, temperature, and inlet-gas composition. The experimental apparatus consisted essentially of an insulated resistive-heated tube furnace. The gap between the tube and the balance box was sealed by means of flexible rubber bellows. A high-grade alumina pedestal, which was connected to the balance mechanism, was used for the transmission of changes in mass, and as a support for the sample crucible when the crucible was raised into the pre-calibrated hot zone of the furnace. The hot zone was maintained at the pre-selected temperature by means of a programmable furnace controller, which utilized the milli-volt output from a suitably positioned thermocouple.

In order to improve the contact between the inlet gases and the test pellets, slots to provide several entry points for gas were cut in the bases and sides of the alumina crucibles (of 30 mm diameter and 48 mm height) by means of a diamond-coated cutting wheel. Calibration curves of volumetric flowrate versus rotameter setting were produced for carbon mon-oxide and carbon dioxide, and the rotameter values were calculated to give a total flowrate of 1.3 ℓ/min, irrespective of the composition of the gas. The CO/CO_2 ratios of the gas entering the furnace were confirmed by use of a Leybold-Hereaus Binos-1 infrared gas analyser.

The pellets to be tested were made from materials (Table I) that had been milled to a nominal particle size of 75 per cent passing 200 mesh (74 μm). Batches of material were pre-weighed, tumble-mixed for 10 minutes, and then pelletized on a disk of 0.6 m diameter. The prepared pellets were then oven-dried at 120°C for 12 hours. In some instances, finer raw materials were used, namely 100 per cent smaller than 74 μm and 80 per cent smaller than 44 μm (see Table II).

Metallization Tests on Uncoated Pellets

The initial experimental runs were carried out using pellets of two compositions, R1A and R2A (Table II). R1A is the 'standard' recipe for fluxed pellets that is used at Mintek. This recipe allows for ratios of chromite to total flux of 100:20 and of chromite to anthracite of 100:30. As a result, the pellet has a carbon content that is 15 per cent in excess of the stoichiometric amount required for the total reduction of the iron and chromium oxides and the formation of chromium and iron carbides reduced from the chromite. The second recipe (R2A) was designed to produce a pellet with a chromite-to-anthracite ratio somewhat lower (100:50). This would allow the effect of the increased excess carbon on the production of carbon monoxide by the Boudouard reaction,

$$C_{(pellet)} + CO_{2(combusted\ gas)}$$

$$\rightarrow 2CO_{(product\ gas)}$$
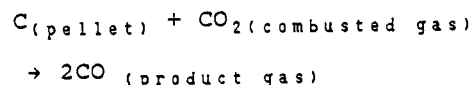
$$(\Delta G_T^0 = 171 - 0.174T \text{ kJ/mol}),$$

and thus the pre-reduction process itself to be investigated.

All the initial experiments were carried out for 3 hours at 1300°C. Simulated gases with compositions that essentially covered the extremes of combustion conditions namely reducing conditions (uncombusted 100 per cent carbon monoxide) and oxidizing conditions (totally combusted 100 per cent carbon dioxide) were used, (Table III). The reaction time of 3 hours was chosen as being representative of the rotary-kiln process.

Subsequent tests were carried out in an effort to assess the dependence on time of the degree of metallization of chromium and iron at a selected CO/CO_2 ratio. Pellets based on the R1A recipe were heated under an atmosphere containing 75 per cent carbon monoxide and 25 per cent carbon dioxide for various times up to 3 hours. Two additional types of pellet, R1B and R1C (Table II), based on the R1A recipe, but prepared from raw materials of different particle sizes, were also tested under these conditions.

Results of the Tests on Uncoated Pellets

The results of the metallization tests on uncoated pellets are shown in Figures 1 and 2.

With pellets of the R1A and R2A compositions, high degrees of iron metallization (i.e. more than 95 per cent) were achieved only at carbon dioxide concentrations lower than 5 per cent by volume. Chromium was even more sensitive to the gas composition, and significant degrees of metallization (over 75 per cent) were achieved only in atmospheres of virtually 100 per cent carbon monoxide. At less than 50 per cent carbon monoxide virtually no chromium was metallized after 3 hours. In contrast, the reduction of iron, which is thermodynamically more favourable than that of chromium, becomes somewhat less sensitive to gas composition at carbon monoxide levels above approximately 80 per cent.

The metallization curves for iron and chromium are similar for both types of pellets, and the extra carbon in the R2A pellets was only marginally effective in increasing the degree of metallization at higher concentrations of carbon monoxide.

The results shown in Figure 2 indicate that the degree of metallization of chromium and iron is strongly dependent on time. In the R1A pellets, the degree of metallization reaches a maximum (42 per cent for chromium and 80 per cent for iron) in about 60 minutes, after which it decreases to about 15 per cent for chromium and 50 to 60 per cent for iron after 3 hours.

For R1B and R1C pellets, the extent of chromium and iron metallization after 30 minutes at a CO/CO_2 ratio of 3 (Figure 2) was similar to that for R1A pellets tested under 95 per cent carbon monoxide for 3 hours

(Figure 1). The rate of metallization, however, slowed considerably after about 30 minutes, indicating that the conditions for reduction had become less favourable. This is probably due to the oxidation of the carbonaceous reducing agent in the pellets by carbon dioxide which becomes noticeable only after approximately 30 minutes.

While the rates of metallization of chromium and iron are affected similarly, the time required for the peak metallization of the iron, and particularly of the chromium, differs slightly with differences in the particle size of the raw materials. Figure 2 shows that the maximum metallization of chromium in R1B and R1C pellets, was reached in 50 to 60 minutes, whereas it took 60 to 70 minutes in R1A pellets.

The maximum degree of metallization of chromium and iron in R1B and R1C pellets was considerably higher than that in the standard R1A pellets (56 per cent metallization of chromium in R1C pellets after 1 hour compared with 42 per cent in R1A pellets). The R1B and R1C pellets also underwent a more rapid fall-off in chromium metallization after 1 hour, but nevertheless retained a higher level of metallization of chromium and iron after 3 hours.

Metallization Tests on Coated Pellets

Coatings of various oxides (aluminosilicates), in particular andalusite, and of ferrochromium-metal fines were evaluated as a means by which the ingress of carbon dioxide into the pellet could be minimized[10,11]. It was thought that the coatings would diminish the oxidation of the reducing agent in the pellets, and thus improve the low metallization levels. The coating materials were were ground to 75 per cent smaller than 74 μm, weighed, and mixed with bentonite binder (2 per cent by mass) before being added gradually to the wetted, composite, chromite base-pellets as they tumbled in the pelletizer. The coated pellets were then oven-dried. The coating additions are expressed as the relative mass percentage (RMP), where

$$RMP = \frac{\text{Mass of the coating}}{\text{Mass of the base pellet}} \times 100.$$

The coating additions were chosen such that the pre-sized base-pellets (9 to 10 mm in diameter) were coated

with a ferrochromium layer of about 0,4 mm thickness, or an andalusite layer of about 1 mm thickness, i.e. 36 to 44 per cent of the mass of the pellet. TGA tests were carried out under the same conditions as those used for the uncoated pellets in an effort to establish whether these relatively substantial coatings would prevent oxidation of the reducing agent. If the results were encouraging, the use of thinner coatings would be investigated.

Results of the Tests on Coated Pellets

The results of the metallization tests on ferrochromium-coated and andalusite-coated pellets are shown in Figures 3 and 4 respectively. The degree of metallization has been suitably corrected for the mass of the coating material. A comparison of the results corrected in this manner with the results of tests in which the base pellet alone was leached (i.e. the coating was removed) indicated differences of less than 2 per cent for the metallization of chromium and iron.

The results indicated that a coating of ferrochromium about 0,4 mm in thickness significantly improves the metallization in the base pellet, the degree of metallization of chromium and iron being approximately 72 and 90 per cent respectively, even after 3 hours in an atmosphere consisting of 100 per cent carbon dioxide. The use of an oxidizing atmosphere (100 per cent carbon dioxide) rather than a reducing atmosphere (100 per cent carbon monoxide) decreased the degree of metallization of chromium only slightly (from 84 to 72 per cent). The metallization of iron was almost independent of the gas composition.

Andalusite-coated pellets showed slightly more sensitivity to the CO/CO_2 ratio, but nevertheless attained 58 per cent chromium metallization after 3 hours at $1300°C$ in atmospheres of 100 per cent carbon dioxide. Under less oxidizing conditions, such as a CO/CO_2 ratio of 1, the degree of chromium metallization in andalusite-coated pellets was about 68 per cent as against 77 per cent in ferrochromium-coated pellets.

Subsequent tests, in which thinner ferrochromium coatings with lower RMP values (10 per cent) were used, yielded similar results. The degree of metallization of chromium and iron attained after 3 hours at $1300°C$ under an atmosphere of 100 per cent carbon dioxide was 60 and 88 per

cent respectively. The scope for optimization of the thickness of the coatings is being investigated.

Mineralogical Investigation

Samples of coated and uncoated pellets that had been tested under each of the gas compositions were examined by energy dispersive spectroscopy (EDS) using a scanning electron microscope (SEM).

Pellets Without Coatings

Essentially no residual carbon was noted in any of the samples tested for 3 hours under atmospheres containing more than 50 per cent carbon dioxide. The reacted pellets generally has a porous structure, with islands of flux containing grains of unaltered chromite or partially altered chromite (PAC) (Figure 5).

Generally, the effect of the flux appeared to be more pronounced for samples tested under higher levels of carbon monoxide (50 per cent and above), substantial dissolution of the chromite grains being observed. At less then 50 per cent carbon monoxide, the degree of breaking-up and dissolution of the chromite particles was not significant. These observations confirm the interdependence of dissolution and low partial pressure of oxygen reported in earlier work[7].

The poorly metallized samples were characterized by isolated regions in the microstructure containing small metal blebs (5 to 10 μm), which were shown by SEM-EDS analysis to consist essentially of iron containing 4 to 5 per cent chromium. The reoxidation products were euhedral $MgO.(AlCr)_2O_3$ spinel crystals and $Cr_2O_3.Al_2O_3$ sesquioxide laths. These features are also evident in Figure 5.

R1A pellets exhibited shrinking-core effects. A relatively dense but less metallized region which was not present after 1½ hours, was noted in the centre of each pellet after 1 hour (Figure 6). The core was characterized by an increased content of residual anthracite and a decreased content of sesquioxide. The sesquioxide forms by direct oxidation of the ferrochromium blebs (Figure 7), and is usually found in association with recrystallized spinel crystals. The presence of more anthracite and less sesquioxide in the inner (core) region of the pellet is indicative of more-reducing conditions. An examination of R1A pellets tested for 3 hours revealed no cores and an even distribution

of sesquioxide, indicating that the effect of the carbon dioxide in causing insufficiently reducing conditions and reoxidation proceeds fairly slowly at practical CO/CO_2 ratios, and becomes significant in rate only after 1 to 1½ hours. The metallization curves (Figure 2) support this interpretation.

These features indicate that the degree of metallization after about 1 hour is controlled by the internal partial pressure of carbon monoxide which is, in turn, a function of the residual carbon content. Since a shrinking-core effect is indicated, the rapid fall-off in metallization after 1 to 1½ hours is to be expected because of the relationship between the shrinking volume of the core and the residual carbon content.

A further important factor is the extent of sintering and shrinkage of the pellet, which was found to be strongly dependent on the particle-size distribution of the starting material. Higher degrees of sintering can occur in the finer materials, which, having lower porosity, afford the metallic material more protection against the ingress of carbon dioxide.

Coated Pellets

SEM examination of coated pellets indicated that, while the overall sealing mechanisms of the two types of coating was similar, the metallic and oxide materials formed effective protective skins by different mechanisms.

The ferrochromium coating consisted of an inner layer of sintered ferrochromium grains surrounded by a silicate phase, a thin (some 50 to 100 μm) intermediate layer containing lath-shaped chromic oxide crystals and a few recrystallized spinel grains, and a dense, continuous outer sealing layer of $Cr_2O_3.Al_2O_3$ sesquioxide containing up to 50 per cent alumina. This morphology was noted in pellets tested under all gas compositions except 100 per cent carbon monoxide. The SEM micrographs in Figures 8 and 9 show the coating and the highly metallized base pellet.

Pellets coated with ferrochromium appear to rapidly form a continuous outer film, which, although only 25 to 50 μm thick, probably plays an important role in sealing the pellet and preventing the ingress of the carbon dioxide in the furnace atmosphere. Generally, only a small uneven shrinkage gap (an indication of the initial rate at which the carbon was oxidized by carbon dioxide) formed in ferro-

chromium-coated pellets, suggesting that carbon dioxide can penetrate to the core of the pellet only during the first few minutes of the experiment. Once the protective skin or veneer of silicate has formed, metallization can proceed in the inner core of the pellet, even at 100 per cent carbon dioxide, without the subsequent reoxidation shown by the uncoated pellets after 60 to 90 minutes.

Andalusite-coated pellets contained two distinct zones: an inner, dense, well-sintered zone (some 150 to 200 μm thick) in which mullite $(3Al_2O_3.2SiO_2)$ formed, and a porous outer layer (250 to 300 μm thick) exhibiting less sintering and higher porosity (Figure 10). The cores of these coated pellets tended to exhibit slightly more shrinkage than did those of the ferrochromium-coated pellets, and the reaction was slightly more sensitive to the proportion of carbon dioxide in the atmosphere. The formation of the dense inner layer of the coating appears to be somewhat dependent on the reaction between the flux, the bentonite, and the coating material, which undergo partial (or complete) transformation to mullite and silicate glass. The inner coating of these pellets also appears to form more slowly than the outer oxide skin on the ferrochromium-coated pellets.

Both types of coating showed hairline cracks, probably due to internal gas pressure or shrinkage.

THE POTENTIAL COMMERCIAL APPLICATION OF FLUXED AND COATED PELLETS

In any consideration of the commercial application of fluxed and coated chromite pellets, the properties and the cost of the coating are important factors.

Properties of the Coating

For the pre-reduction of coated composite pellets in, for instance, a shaft-kiln operation, the experimental work indicated that the following coating properties are desirable.
(1) The coating should be chemically inert. Metallic coatings should be resistant to oxidation, while oxide coatings should be refractory but still allow rapid sintering.
(2) The volume of the coating should be stable, i.e. the coating should have a low coefficient of thermal expansion. This requirement precludes the use of several otherwise suitable materials, such as dolomite or

limestone, which undergo volume changes due to dehydration and decarbonation.

(3) The coating must not react too readily with the calcium fluoride, feldspar or silica components of the flux.

(4) Compatibility of the coating with downstream processing is important. For example, the constraints on the electrical resistivity of the burden and the composition of the slag must be satisfied.

(5) The material should have a low porosity and, particularly, permeability.

(6) The coating should adhere well to the core of the pellet during pelletization.

(7) The material should be of adequate strength and toughness to withstand shock loading and internal gas pressure, which may burst the coating. (Up to 0,6 litres of carbon monoxide can be generated at standard temperature and pressure in 1 hour by a single pellet of 10 mm diameter.)

Coating Costs

The use of coated pellets would have a potentially net positive effect on process costs, since it would allow pre-reduction to be carried out at very low CO/CO_2 ratios, thereby allowing for the complete combustion of the fuel and the carbon monoxide generated by the reduction reactions. Furthermore, the coating also prevents reoxidation of the metallized material that forms during the pre-reduction stage. Higher degrees of pre-reduction result in a lower consumption of electrical energy per ton of ferrochromium in the downstream furnace.

The benefits, in terms of the lower PF requirements, afforded by the use of fluxes and coatings were calculated from mass and energy balances that were carried out using the PYROSIM simulation computer program. The program, which was developed at Mintek[12], employs the technique of free-energy minimization using known thermodynamic data[13]. A brief description of the process model is given in Appendix B. The model uses the more-general term of *pre-reduction* rather than *metallization* to take into account the reduction of trivalent iron to the divalent form, the content of which can vary in individual chromites.

Three types of pellet were considered: an unfluxed chromite-anthra-

cite pellet with a chromite anthracite ratio of 100:30, the standard uncoated (R1A) fluxed pellet, and an R1A fluxed pellet coated with a 10 per cent RMP ferrochromium coating. A plant producing 60 kt of alloy per annum was considered.

Figure 11 shows the relationships between the mass of PF required per ton of alloy, and the percentage reduction for two chosen CO/CO_2 ratios, namely zero and 1.0. Point A depicts a good level of pre-reduction (60 per cent) for an uncoated unfluxed pellet. The PF requirement is 0.83 t per ton of alloy for an off-gas temperature of 1000°C and a CO/CO_2 ratio of 1.0. Point B shows the predicted metallization of 80 per cent for a fluxed pellet but, because it is uncoated, the outside of the pellet is partly oxidized and therefore exhibits a lower degree of metallization (65 per cent) at point B'. The PF requirements for points B and B' are 0.76 and 0.71 t per ton of ferrochromium respectively.

Point C shows the prediction for a coated-and-fluxed pellet. The PF requirement can be seen to be virtually independent of the degree of pre-reduction since, under a carbon dioxide atmosphere of 100 per cent, all the carbon monoxide generated by the reduction reactions can be combusted and, the higher the degree of reduction, the more carbon monoxide is produced. The predicted PF requirement is only 0.31 t per ton of ferrochromium, and the expected degree of pre-reduction is 80 per cent. The energy cost will therefore be about US$50 lower per ton of ferro-chromium for this pellet than for an unfluxed uncoated pellet (i.e. about $20 per ton of pellets). The overall flux and coating contents of the coated pellet would be 12 and 9 per cent respectively (21 per cent total), representing a combined cost saving of about $80 per ton of fluxes and coating materials. This figure excludes any further benefits that would result, such as increased output and saving in PF utilization through the use of the off-gas from a downstream smelter-gasifier process.

The production of ferrochromium fines is an unavoidable aspect of the sizing and handling of ferrochromium alloy. The use of these fines in coatings is therefore essentially a recycling operation, and the only significant cost would be that associated with milling.

The Selection of Appropriate Unit Operations

Three potential unit operations should be considered for the processing of fluxed or fluxed-and-coated pellets. These are rotary-hearth furnaces, rotary kilns, and shaft kilns.

The rotary-hearth furnace, which was developed for the production of direct-reduced iron (DRI) has potentially the lowest residence time, and can be described as being 'heat-transfer driven', since there is no external pre-heating of the charge, and the pellets are heated rapidly to the operating temperature[8]. Also, the physical properties of the pellets, particularly their green strength, impact resistance, abrasion resistance, and resistance to softening, are probably not as critical for this process as for other processes, since the depth of the pellet bed is only 1 to 2 pellet diameters, and no tumbling action is involved. This route favours a 'high' flux content of up to 20 per cent by mass of chromite to maximize the reduction rate. The need for a protective coating on the pellets, even at a relatively high CO/CO_2 ratio of 3 in the process gas, is questionable because of the relatively slight gas-solid contact. Nevertheless, pilot-plant testwork is recommended to allow unfluxed pellets to be compared with fluxed and fluxed-and-coated pellets.

The rotary-kiln process developed for the pre-reduction of chromite operates at a higher temperature (1400°C) than would a shaft kiln (1300°C) and has a significantly longer retention time than the rotary-hearth furnace. The physical properties of the pellets are critical[14,15], and careful attention must be paid to the particle size distribution, binder type and content, and final moisture content of the pellet. An induration stage is normally included so that the sensible and chemical energy of the kiln off-gas can be utilized. The rotary kiln has potentially a higher maximum throughput than the rotary-hearth furnace in terms of scale, but this is dependent on the control of dam-ring formation and pre-reduction level. CO/CO_2 ratios in the process gas are generally lower than those for the rotary-hearth furnace (0,5 to 1,0). This unit operation probably requires a lower flux content (10 to 15 per cent by mass of chromite) to minimize the possibility of pellet sticking and ring formation, and to ensure that the necessary strength

critera are satisfied.

The shaft kiln has the lowest potential capital outlay because of the relative simplicity of its mechanical and civil construction, and its lower maintenance cost. Lower operating temperatures are indicated as a measure to avoid cluster formation in the bed. To ensure that the pellets will be sound after reduction, a low flux content (approximately 10 per cent by mass of chromite) is envisaged. In addition the hot combusted gases must be introduced carefully to maximize the use of sensible heat while avoiding flame impingement on the pellets in the combustion zone. The packed-bed unit operation is more efficient in terms of utilization of the available bed volume than are the rotary-hearth furnace and rotary kiln, and the thermal efficiency of the shaft-kiln countercurrent operation is a function of the temperature distribution through the height of the bed (i.e. the temperature differential between the inlet and outlet gases). The use of pellet coatings, together with a high utilization of the sensible heat of the heating gas, would ensure high fuel efficiency, particularly since the process is not limited by the CO/CO_2 ratio in the process gas, and because complete combustion of the fuel and the reaction product gas up to CO/CO_2 ratios of less than 0,01 can be achieved. In small-scale pilot-plant work, it has also been found that pellet coatings minimize clustering by preventing contact between the fluxed base pellets, and improve the impact and compressive strength of composite pellets.

CONCLUSIONS

In a commercial operation, several potential benefits could be realized as a result of the enhanced reduction kinetics, either alone, or in combination with coatings. Thus savings in energy would be achieved, and high pre-reduction levels retained.

The laboratory work has indicated that, under the moderately oxidizing range of CO/CO_2 atmospheres studied (i.e. 3:1), the higher degree of metallization attained by use of fluxed uncoated pellets in contact with the gas phase is strongly time-dependent, and that the choice of unit operation is limited to those in which a rapid throughput (residence time less than 60 minutes) can be realized. With coated pellets, however, the

CO/CO_2 ratio and hence time restrictions are removed. Advantage can thus be taken of the counter-current gas-solid characteristics of the shaft-kiln process with its concommitantly higher fuel efficiency (due to the complete combustion of carbon monoxide to carbon dioxide and lower off-gas temperature).

The enhanced reduction rates afforded by the fluxes can be utilized in several ways. For example, for an existing unit operation, the output can be increased at the same operating temperature, or a similar output can be achieved at a lower operating temperature. For a new plant, the same output can be attained by the use of a smaller furnace. Thus savings in operating costs and/or capital expenditure can be realized.

When the degree of metallization in the pre-reduced pellets is high, only a melting operation is needed subsequently. Hence, the electrical energy requirement is reduced from about 4000 kW.h per ton of ferrochromium (for 100 per cent smelting) to about 1600 kW.h per ton of ferrochromium depending on the degree of pre-reduction. The downstream processing units considered could include a d.c. plasma-arc furnace using an open-bath configuration, or a slag-resistance process, neither of which has the constraints imposed by the electrical resistivity of the burden as is the case for the conventional the submerged-arc furnace[8,16]. Furthermore, a smelter-gasifier or converter could be used to melt the highly reduced pellets. These processes would also generate gas for the pre-reduction unit in which the coated pellets would be reduced, thereby substantially reducing the PF requirement.

ACKNOWLEDGEMENTS

This paper is published by permission of the Council for Mineral Technology (Mintek). The authors wish to record their gratitude to Messrs W.F.A.T. Meihack and R.T. Jones for their assistance in carrying out the simulation work, and to Mr P. Language for his assistance with the experimental work. The support of Messrs R.A. Featherstone and S.S.J. Johansson of Samancor Limited is acknowledged with thanks.

REFERENCES

1. H. Kammeyer, G. Pugh, and K.U. Maske, "Open-bath Production of Ferrochromium in a d.c. Plasma Furnace," INFACON '89, New Orleans, Louisiana, April 1989.

2. A. Wikander, "The Plasma-Chrome Process at Swede Chrome AB," INFACON '89, April 1989, New Orleans, Louisiana.

3. T. Arai, et al., "Results of Smelting Reduction Test to Make Stainless Steel by Industrial Furnace," Transactions of the Iron and Steel Institute of Japan., Vol. 28, 1988, p. B-45.

4. H. Dorr, et al., "Process for the Production of Ferrochromium," S.Afr. Pat. 84/10101, December 28th, 1984, pp. 1-28.

5. J.E. Gomersall., "MS&A - Steeling Itself for the Future" Barlows '88 periodical, Vol. 1, 1988, pp. 11-12.

6. D.P. O'Shaughnessy, M. Sciarone, and H.E. Bartlett, "Ferrochrome Production via the Pre-reduction Route," South African Institute of Mining and Metallurgy Pyrometallurgy Vacation School, Johannesburg, April 1981.

7. N.F. Dawson and R.I. Edwards, "Factors Affecting the Reduction Rate of Chromite," INFACON 86, Proceedings of the 4th International Ferro-alloys Congress, Associacao Brasileira dos Produitores de Ferro-Ligas - Abrafe, Sao Paulo, 1986, pp. 105-113.

8. G. Rath, T. Vlajac, and W. Hofmann. "Production of Sponge Iron and Highly Metallized Manganese and Chrome Ore Pellets Employing the Rotary Hearth Furnace (RHF) as well as Smelting into Pig Iron, Steel and Ferro Alloys," TECHNOGERMA INDIA '88, German Technical Exhibition, New Delhi, Pragati Maiden, March 14-20, 1988, pp. 1-28.

9. M.J. Niayesh and G.W. Fletcher, "An Assessment of Smelting Reduction Processes in the Production of Fe-Cr-C Alloys," INFACON 86, Proceedings of the 4th International Ferro-alloys Congress, Associacao Brasileira dos Produitores de Ferro-Ligas - Abrafe, Sao Paulo, 1986, pp. 115-123.

10. N.A. Barcza and R.C. Nunnington, "The Thermal Reduction of Agglomerated Metallurgical Feed Materials with Metallic Coatings," S. Afr. Pat. 88/1098, 17th February, 1988, pp. 1-30.

11. R.C. Nunnington, R.A. Featherstone, and N.A. Barcza, "The Thermal Reduction of Agglomerated Metallurgical Feed Materials with Oxide Coatings," S. Afr. Pat. 88/2581, 13th April, 1988, pp. 1-34.

12. R.T. Jones, "Computer Simulation of Pyrometallurgical Processes," APCOM 87, Proceedings of the Twentieth International Symposium on the Application of Computers and Mathematics in the Mineral Industries, the South African Institute of Mining and Metallurgy,, Johannesburg, 1987, Vol. 2, pp. 265-279.

13. THERMFACT (F*A*C*T thermodynamic data base), 447 Berwick Avenue, Mount-Royal, Quebec, Canada.

14. Y. Otani and K. Ichikawa, "Manufacture and Use of Pre-reduced Chromium-ore Pellets," INFACON 74, Proceedings of the First International Ferro-alloys Congress, the South African Institute of Mining and Metallurgy, Johannesburg, 1975, pp. 31-37.

15. H. Saito, et al., "Evaluation of method of Chromium Ore for Solid State Reduction Process (SRC)," Paper presented at INFACON 83, Tokyo, Japan, 1983.

16. N.A. Barcza, "The Development of Large-scale Thermal Plasma Systems," Journal of the South African Institute of Mining and Metallurgy, Vol. 86, No. 8. August 1986, pp. 317-333.

APPENDIX A

LEACHING METHOD AND CALCULATION OF PERCENTAGE METALLIZATION

The leaching-and-analysis technique involved regrinding of the pre-reduced pellets to smaller than 74 μm followed by leaching at approximately 96°C for 12 hours in 37 per cent hydrochloric acid (by mass) diluted in a 50/50 ratio with distilled water. The leach liquor and residue were analysed (for mass-balance purposes) by spectrography using an inductively coupled plasma, and by X-ray-fluorescence techniques, for soluble (metallic) and insoluble (oxidic) chromium and iron species. By use of these analyses, the recorded original and final mass of the sample, the mass leached, and the masses of the residue, the degree of metallization was calculated using the following formulae:

$$\text{Cr metallization } (\% \ M_{Cr}) = \frac{Cr^0}{Cr_{tot}} \times 100,$$

and

$$\text{Fe metallization } (\% \ M_{Fe}) = \frac{Fe^0}{Fe_{tot}} \times 100.$$

The total percentage metallization is defined as

$$M_{tot} = \frac{Cr^0 + Fe^0}{Cr_{tot} + Fe_{tot}} \times 100,$$

where

Cr^0 is the metallic (soluble) chromium (g),

Fe^0 is the metallic (soluble) iron (g),

Cr_{tot} is the total chromium (g) present in the prereduced material, and

Fe_{tot} is the total iron(g) present in the pre-reduced material.

APPENDIX B

THE PRE-REDUCTION UNIT MODEL

The pre-reduction unit (PRU) is semi-empirical, and assumes that true equilibrium does not exist between the gas derived from the combustion of the PF and the composite pellets. It assumes that the PF, the carbon combusted, the carbon monoxide generated within the pellet, and the air reach equilibrium at a specified operating temperature with a resulting overall CO/CO_2 ratio.

The chromium and iron oxide reduction levels are specified in the program input, and are not calculated predictively. The degree of reduction in the pellet input stream fixes the composition of the metal and the remaining oxide phases in the solids stream, and an energy balance between the input and output streams specifies the energy input required to maintain the balance.

A flowsheet of the PRU model is given in Fig. B-1.

The following assumptions and process specifications were made for the PRU model.

(i)   For unfluxed pellets, the heat losses from the kiln are 4500 kW for the operating temperature of 1400°C.

(ii)   Fluxed pellets require a lower operating temperature of 1300°C, so the heat losses are lower (4000 kW). For the lower operating temperature, the off-gas temperature is reduced from 1000 to 900°C.

(iii)   There is no oxidation of the carbon contained in the pellet by the carbon dioxide present in the process gas.

(iv)   There is no pre-heating of the pellets; the pellets, combustion coal, and air are introduced at 25°C.

(v)   The coal ash leaves the kiln at the same temperature as the off-gas.

(vi)   The pellets are discharged at the process temperature.

The term pre-reduction is associated with the removal of oxygen from the oxidic iron and chromium species in the chrome spinel, and is defined as:

% Pre-reduction = Mass of oxygen removed divided by the original removable oxygen in iron and chromium species, and multiplied by 100.

The original removable oxygen per unit mass of chromite ore is therefore dependent on the relative proportions of FeO, Fe_2O_3, and Cr_2O_3, as determined by chemical analysis.

The 60, 65, and 80 per cent pre-reduction levels considered in Figure 11 correspond to iron and chromium reduction levels of 95 and 47, 97 and 54, and 99 and 73 per cent respectively.
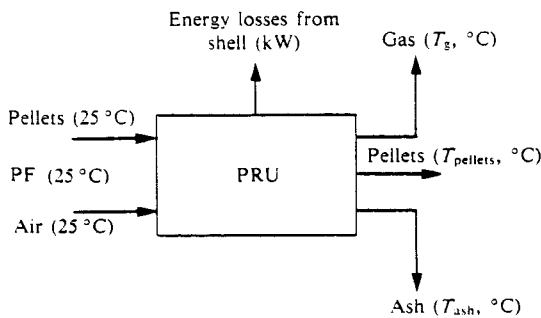

Fig. B-1. The PRU model

TABLE 1. CHEMICAL ANALYSES OF THE RAW MATERIALS USED FOR THE FLUXED, COMPOSITE CHROMITE PELLETS

Material	Constituent, % by mass									
	Cr_2O_3	FeO	Fe_2O_3	Al_2O_3	MgO	SiO_2	CaF_2	Na_2O	K_2O	Fixed carbon
Mooinooi chromite	45.4	19.1	7.85	14.6	9.17	1.02	–	–	–	–
Grinaker anthracite	–	–	0.56	4.46	–	5.86	–	0.33	0.22	77.8
Granite	–	–	1.26	19.0	0.30	71.9	–	4.13	3.91	–
Fluorspar	–	–	–	0.20	–	0.80	97.9	–	–	–
Bentonite	–	–	3.19	18.5	2.90	54.6	–	2.50	0.60	–

TABLE II. RECIPES FOR THE FLUXED COMPOSITE CHROMITE PELLETS

Pellet recipe	Particle size d 50 (weighted mean)	Fineness of grind	Constituent, % by mass					
			Mooinooi chromite	Grinaker anthracite	Granite	Fluorspar	Bentonite	Moisture
R1A	31.8	75% <74 m	65.4 (100)	19.6 (30)	9.8 (20)	3.3 (20)	1.9	10.1
R1B	14.0	100% <74 m	65.4 (100)	19.6 (30)	9.8 (20)	3.3 (20)	1.9	10.6
R1C	13.5	80% <44 m	65.4 (100)	19.6 (30)	9.8 (20)	3.3 (20)	1.9	10.9
R2A	31.8	75% <74 m	56.6 (100)	28.3 (50)	8.5	2.8 (20)	3.8	11.8

Note   The figures in parentheses relate the proportions of anthracite and total flux to chromite

TABLE III. COMPOSITIONS OF THE GASES USED IN THE INITIAL EXPERIMENTS

Gas no.	Composition		
	CO % by volume	CO_2 % by volume	CO/CO_2 ratio
1	100	0	infinity
2	95	5	19 : 1
3	85	15	5.7 : 1
4	75	25	3.0 : 1
5	50	50	1.0 : 1
6	25	75	0.3 : 1
7	0	100	0.0 : 1

TABLE IV. CHEMICAL ANALYSES OF THE RAW MATERIALS USED FOR PELLET COATINGS

Material	Constituent, % by mass						
	Fe_2O_3	Al_2O_3	SiO_2	Fe	Cr	Si	C
Andalusite	1.4	59.8	37.4	–	–	–	–
Ferrochromium fines	–	–	–	36.8	52.2	3.9	7.1
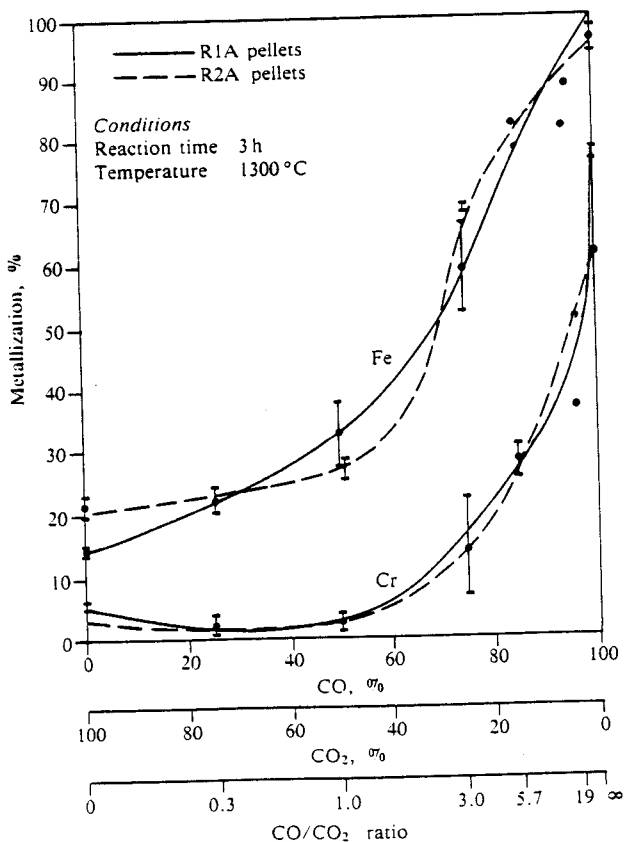
Fig. 1. Effect of the CO/CO_2 ratio on the degree of metallization of chromium and iron in reduced, uncoated R1A and R2A pellets
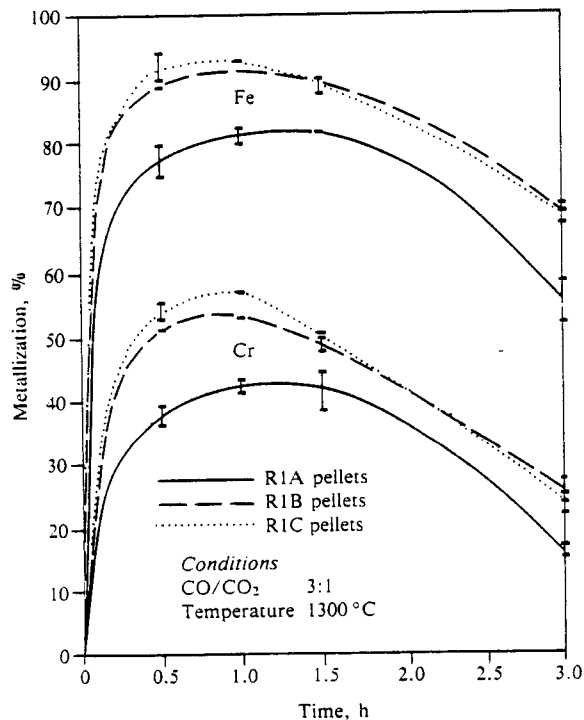
Fig. 2. Effect of reaction time on the degree of metallization of chromium and iron in reduced, uncoated R1A, R1B, and R1C pellets

Author(s) name(s) Nunnington/Barcza

Page # 11 of 14
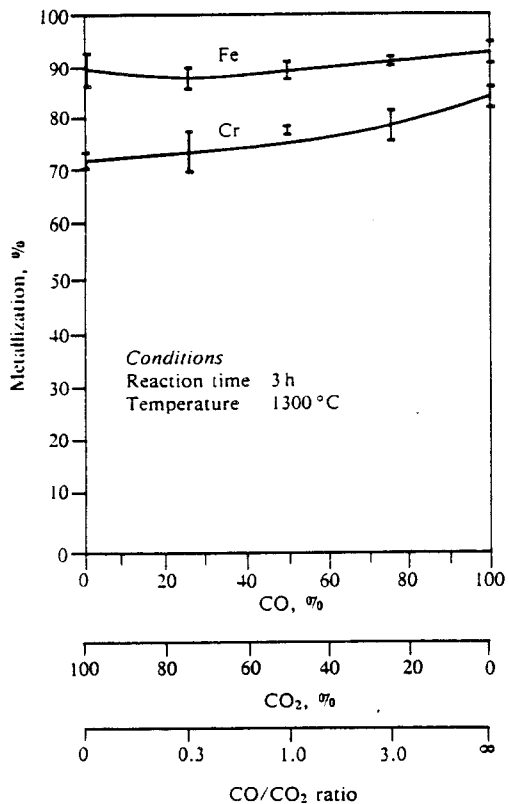
Fig. 3. Effect of the CO/CO₂ ratio on the degree of metal-
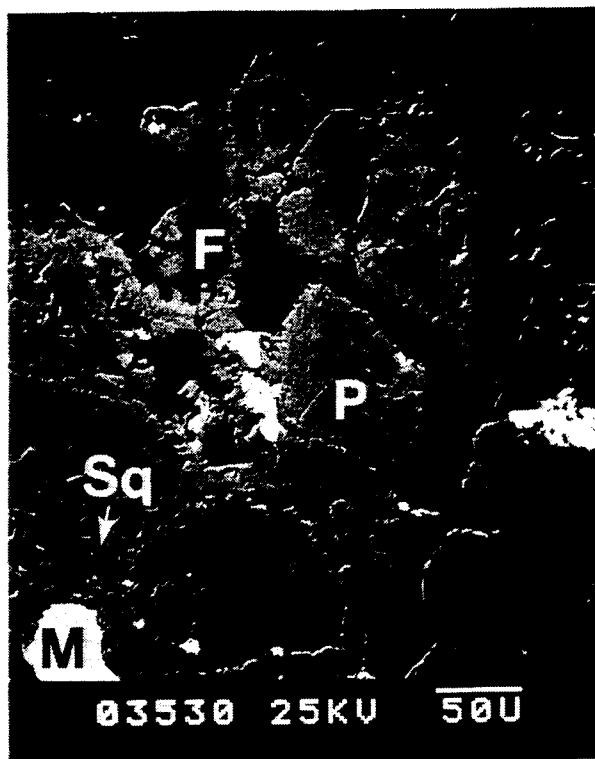lization of chromium and iron in reduced,

Fig. 5. SEM micrograph of an R1A pellet tested at a CO/CO_2 ratio of 1. Only
a few isolated metal blebs can be seen, together with partially altered
chromites that have undergone only limited flux attack.
P   Partially altered chromite particles
Sq $Cr_2O_3 \cdot Al_2O_3$ sesquioxide
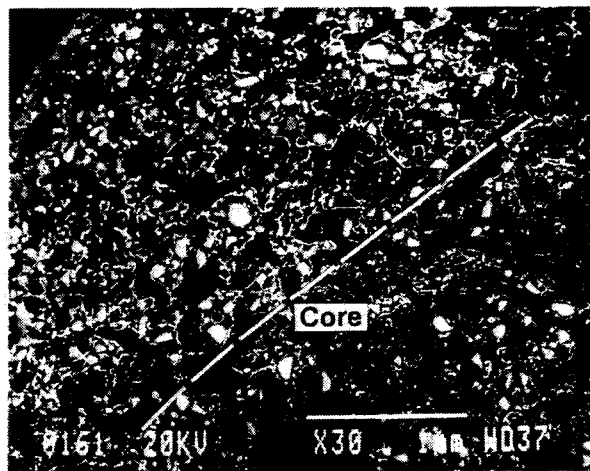F   Altered flux
M   Metal blebs

Fig. 4. Effect of the CO/CO₂ ratio on the degree of metal-
lization of chromium and iron in reduced, andalusite-
coated R1A pellets

Fig. 6. SEM micrograph of an uncoated R1A pellet tested at a CO/CO_2
ratio of 3 for 1 hour at 1300 °C. The boundary between the less
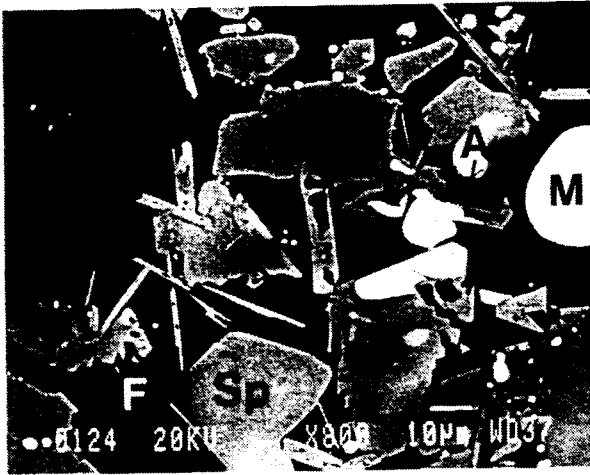metallized core and the outer region of the pellet is indicated

Author(s) name(s) Nunnington/Barcza

Fig. 7. SEM micrograph of the outer region of an R1A pellet tested at a CO/CO_2 ratio of 3 for $1\frac{1}{2}$ hours at 1300 °C. The formation of the sesquioxide by the direct oxidation of the ferrochromium blebs can be seen at point A
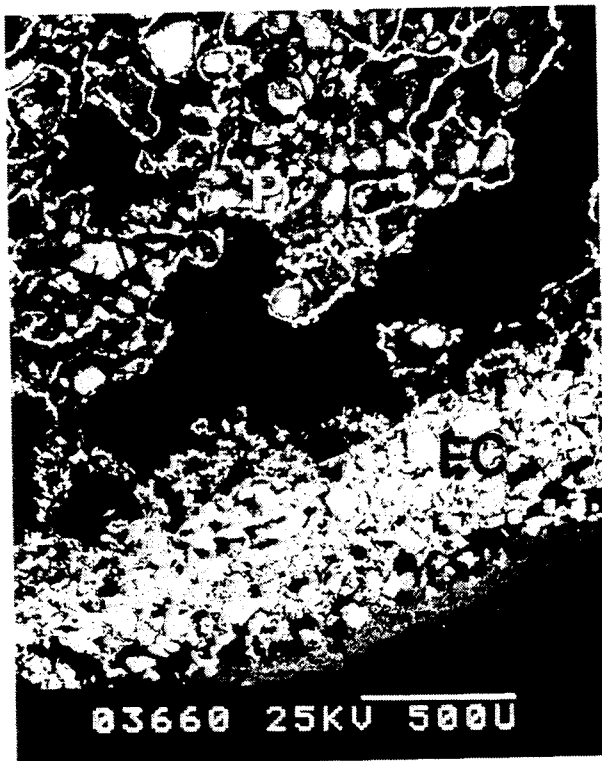

Fig. 8. SEM micrograph of a ferrochromium-coated R1A pellet tested at a CO/CO_2 ratio of 1 for 3 hours at 1300 °C. The boundary between the highly metallized base pellet (P) and the ferrochromium coating (FC) is clearly indicated
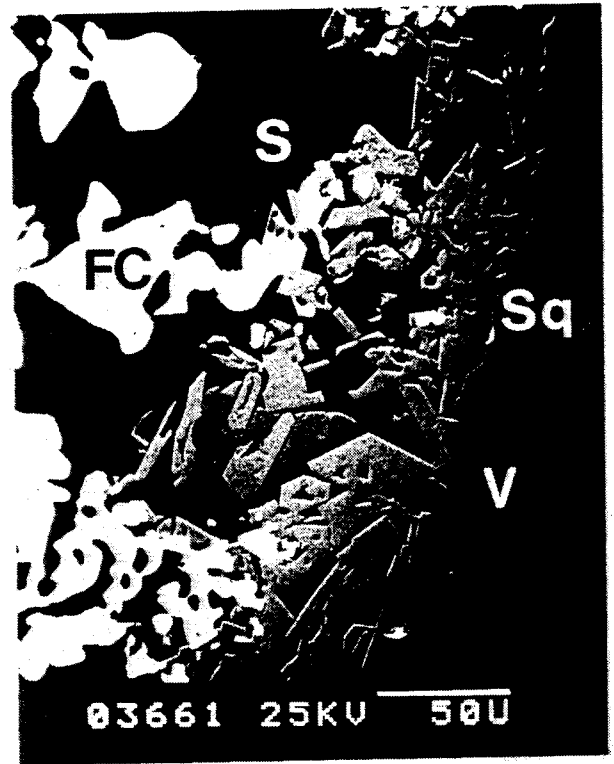

Fig. 9. SEM micrograph showing the outer layers of the ferrochromium coating in more detail.
FC Original ferrochromium
S   Silicate
C Cr_2O_3 crystals containing MgO and Al_2O_3
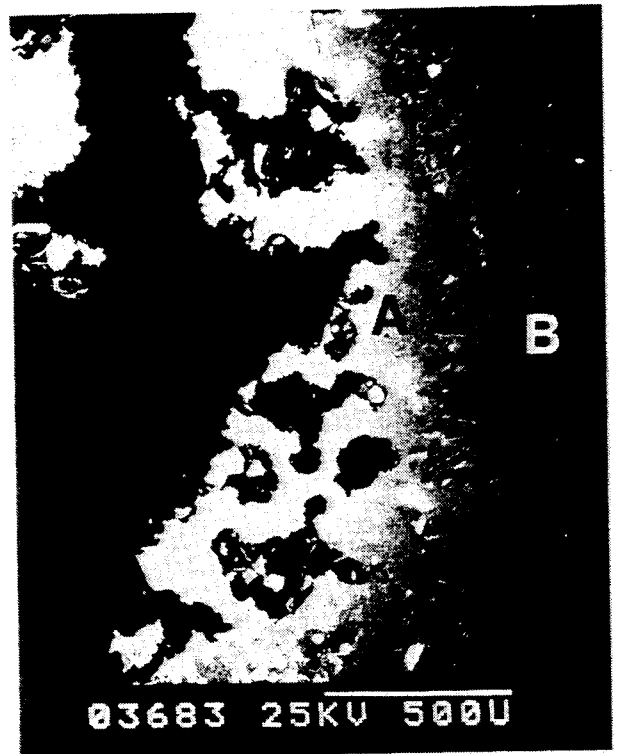Sq $Cr_2O_3 \cdot Al_2O_3$ sesquioxide layer
V   Outer veneer of silicate

Fig. 10. SEM micrograph of an andalusite-coated R1A pellet tested under a 100 per cent CO_2 atmosphere ($CO/CO_2 = 0$) for 3 hours at 1300 °C. The dense inner zone (A) and the open-textured outer zone (B) are indicated
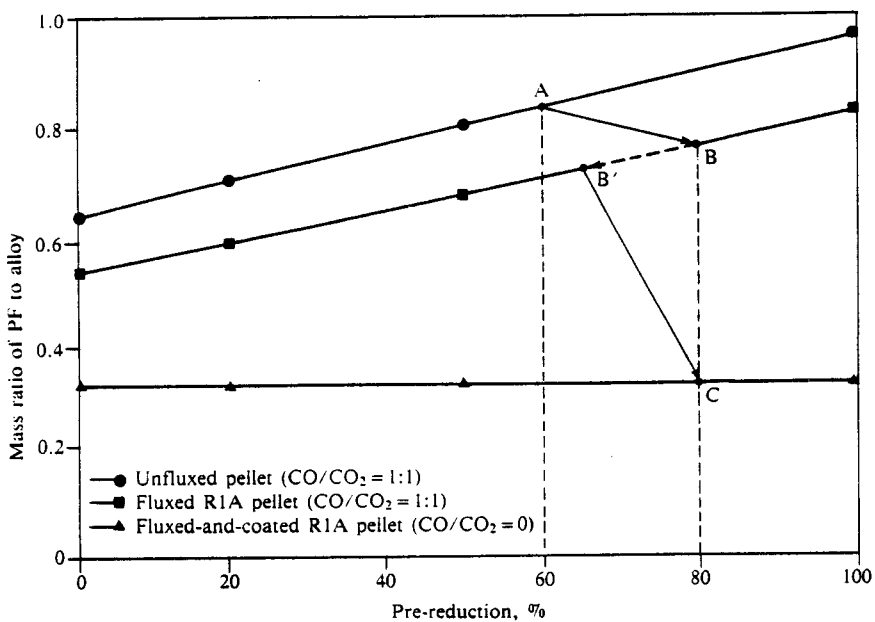
13   14

Fig. 11. Mass ratio of pulverized coal (PF) to ferrochromium required for varying levels of pre-reduction of unfluxed, fluxed, and fluxed-and-coated composite chromite pellets