The prereduction and smelting of chromite concentrate of low chromium-to-iron ratio

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SYNOPSIS

The prereduction and smelting characteristics of UG-2 ore were studied and compared with those of Winterveld chromite ore. The UG-2 ore proved more reducible, and substantial prereduction (over 70 per cent reduction after 30 minutes at 1250 °C) was obtained.

No difficulty was experienced in the production of a high-carbon ferrochromium alloy containing 48 to 50 per cent chromium. Calculations of the energy balance show that UG-2 chromite has lower total energy requirements (both on the basis of unit of ferrochromium produced and of total chromium content). More than 50 per cent of the energy required for reduction can be supplied outside the smelting furnace.

SAMEVATTING

Die voorreduksie en uitsmelteienskappe van UG-2-erts is bestudeer en met die van die Winterveld-chromieterts vergelyk. Die UG-2-erts was meer reduksiebaar en aansienlike voorreduksie (meer as 70 persent reduksie na 30 minute by 1250 °C) is verkry.

Daar is geen probleem ondervind om 'n hoëkoolstof-ferrochroomlegering met 48 tot 50 persent chroom te produseer nie. Energiebalansrekenings toon dat UG-2-chromiet laer totale energie-behoeftes het (sowel per eenheid ferrochroom geproduseer as op die basis van die totale chroominhoud). Meer as 50 persent van die energiebehoeftes vir reduksie kan buite die uitsmeltoond voorsien word.

Introduction

The Upper Chromitite Layer (UG-2) is the uppermost of 13 chromite seams in the Bushveld Complex. There are two main reasons for interest in the UG-2 layer. The first is its size, for the UG-2 represents some 20 per cent of South Africa's known chromite reserves, which in 1980 amounted to about 80 per cent of the world's reserves. The second reason is the presence of platinum-group metals (PGM) in the ore.

Exploitation of the UG-2 will include the recovery of the PGM, which Buchanan[1] estimates as amounting to more than 3,7 Gt of ore at a PGM grade of 8,7 g·t⁻¹. This grade is comparable with that of the Merensky Reef, which is South Africa's main source of PGM at present.

A recent statement by the Lonrho group[2] announced plans for the production of some 4000 kg of PGM annually from the UG-2 Reef. The plant became operational in 1982, and the production of PGM-rich concentrate should generate some 240 kt of 42 per cent Cr_2O_3 chromite tailings with a chromium-to-iron ratio of 1,35. Potentially, this could be converted annually to 120 kt of high-carbon ferrochromium with a chromium content of 50 per cent. This amount of ferrochromium is sufficient to make a significant impact on the ferro-chromium industry. The suitability of the UG-2 reef for the production of an acceptable grade of ferrochromium is of interest not only to existing ferrochromium producers, but also to companies that are potential producers by virtue of their commitment to the recovery of PGM.

The UG-2 chromites differ from other Transvaal chromites in having a lower chromium-to-iron ratio, due mainly to a higher content of iron rather than to a lower content of chromium. A typical UG-2 concentrate has the following analysis (in percentages):

Cr_2O_3	42,2 to 42,9
FeO	17,7 to 18,2
Fe_2O_3	10,6 to 10,9
MgO	9,3 to 10,4
Al_2O_3	15,6 to 15,8
SiO_2	2,3 to 3,3

The ratio of chromium to iron is 1,35, and the molecular formula can be expressed as

$$(Fe_{0,5}^{2+} Mg_{0,5}) (Cr_{1,1} Fe_{0,3}^{3+} Al_{0,6})O_4.$$
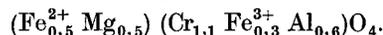
Chromium in the metallurgical industry is mainly used as an alloying element for steel or in the manufacture of stainless steel. In either case, the chromium is normally used in the ferro-alloy form. By far the largest consumption is of high-carbon alloy with a chromium content of 50 to 55 per cent (previously known as charge chrome).

It has been felt (rather than categorically stated) that UG-2 chromites are not suitable for the production of this high-carbon ferrochromium, but a simple calculation shows that ferrochromium with a chromium content of 50 per cent (with 10 per cent carbon plus silicon) can be produced from an ore with a chromium-to-iron ratio of 1,35, even if the chromium recovery is only 93 per cent of the iron recovery. This can be achieved with a slag having 5,7 per cent Cr_2O_3 and a slag-to-metal ratio of 1,33.

A further interesting feature of UG-2 chromites is the fineness of the concentrate (99 per cent of the particles smaller than 300 μm), which makes some form of agglomeration essential. The size grading favours pelletization rather than briquetting. The high proportion of fines

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(80 per cent of the particles smaller than 150 μm) would reduce milling costs since successful pelletization requires a particle size[3] of 85 per cent smaller than 75 μm.

The importance of the UG-2 Layer and the lack of fundamental data on the behaviour of its ore during processing to high-carbon ferrochromium led to the initiation of a project aimed at an examination of the following aspects.

(1) Is extensive solid-state prereduction of the agglo-merated ore possible?
(2) Are there any particular difficulties in the smelting of highly reduced material for the production of ferrochromium?
(3) What grade of alloy can be produced?
(4) Are there any particular advantages or disadvantages in the production of high-carbon ferro-chromium from UG-2 chromites?
(5) Are there any signs of abnormal behaviour that could affect the processing of this material on an industrial scale?

Experimental Techniques

Reduction Tests

Reducibility was tested by thermogravimetric analysis, coupled with gas chromatography for the analysis of the reaction products. The experimental apparatus has been described by Barnes and Finn[4]. All the testwork was conducted under an atmosphere of deoxidized argon.

Smelting Tests

The preliminary work, which was aimed at an evaluation of the effects of slag composition, was con-ducted in an 18 kW radio-frequency (500 kHz) induction furnace. In later tests, use was made of a 50 kW (3 kHz) induction furnace. Both these units have been described by Barnes and Finn[5].

Chemical Analyses

All the chromium-bearing materials, except the prereduced ores, were analysed by optical-emission spectrography (OES) using an inductively coupled plasma source[6]. The carbon and sulphur concentrations were determined by standard combustion techniques.

Ensuring that the carbides were taken into solution quantitatively without the dissolution of chromium and iron oxides presented a problem with the prereduced chromite ores. An unpublished dissolution method, developed by the Johannesburg Consolidated Investment Co. Ltd[7] for their work on prereduced chromites, was used with the Company's permission. After being crushed and ground to 100 per cent smaller than 75 μm, the pre-reduced chromites were boiled under reflux for $1\frac{1}{2}$ hours at 120 °C in a mixture of 10 per cent phosphoric acid and 40 per cent sulphuric acid. This dissolved the metal and carbide, leaving the oxides virtually undissolved. When unreduced chromites were leached, 2 per cent of the chromium and 8 per cent of the iron oxides were found to dissolve, and this was compensated for in the analysis of the results. After filtration, the chromium and iron in the filtrate (metallic and carbide) and in the residue (oxides) were determined by OES.

Terms Used and Preliminary Calculations

The terms *degree of reduction* and *metallization* have not been as well-defined for the reduction of chromite as they have been for the reduction of iron ore, and the definitions used by various investigators have usually reflected the experimental techniques used. Since reduction is associated with the removal of oxygen and the thermogravimetric technique used in this study measures mass loss, reduction (R) is defined as

$$R(\%) = \frac{\text{Mass of oxygen removed}}{\text{Original removable oxygen}} \times 100.$$

Where solid carbon is the reducing agent, carbon monoxide is the reaction product (as will be shown later) and therefore reduction can also be defined as

$$R(\%) = \frac{\text{Mass of CO evolved}}{28/16 \times \text{original removable oxygen}} \times 100.$$

The amount of removable oxygen is determined from chemical analyses of the ores as the oxygen associated with Fe_2O_3, FeO, and Cr_2O_3.

Metallization (M) is defined as

$$M(\%) = \frac{Cr^0 + Fe^0}{Cr_{tot} + Fe_{tot}} \times 100,$$

where Cr^0 = metallic chromium,
$\quad Fe^0$ = metallic iron,
$\quad Cr_{tot}$ = total chromium
$\quad Fe_{tot}$ = total iron.

The relationship between metallization and reduction is not linear because of the following factors.

(1) In the early stages of reduction, Fe_2O_3 is reduced to FeO without any metallization:
$$Fe_2O_3 + C \rightarrow 2\ FeO + CO.$$
(2) FeO is reduced to Fe, producing 1 mol of CO for every mole of Fe produced $(M = R + k_1)$:
$$FeO + C \rightarrow Fe + CO.$$
(3) Cr_2O_3 is reduced to Cr, producing 1,5 mol of CO per mole of Cr produced:
$$Cr_2O_3 + 3\ C \rightarrow 3\ CO + 2\ Cr.$$
$$M = 2/3R + k_2,$$

where k_1 and k_2 are constants relating to the contents of ferric iron and total iron respectively. Since complete oxygen removal corresponds to complete metallization, 100 per cent reduction corresponds to 100 per cent metallization.

Stoichiometric carbon was regarded as the carbon required for complete reduction of the chromium and iron oxides as well as the carbon for the formation of the Fe_3C and Cr_7C_3 carbides.

Results of Reduction Tests

Effect of Time and Temperature

Two samples of ore from different orebodies in the UG-2 Layer were investigated. These are designated CW and CP for the purposes of identification.

Eight isothermal runs were conducted on CW ore at temperatures between 1000 and 1300°C, and eight runs on CP ore at temperatures between 1050 and 1400°C. The results are shown in Figs. 1 and 2 for CW and CP ores respectively. Ore CW shows a higher rate of
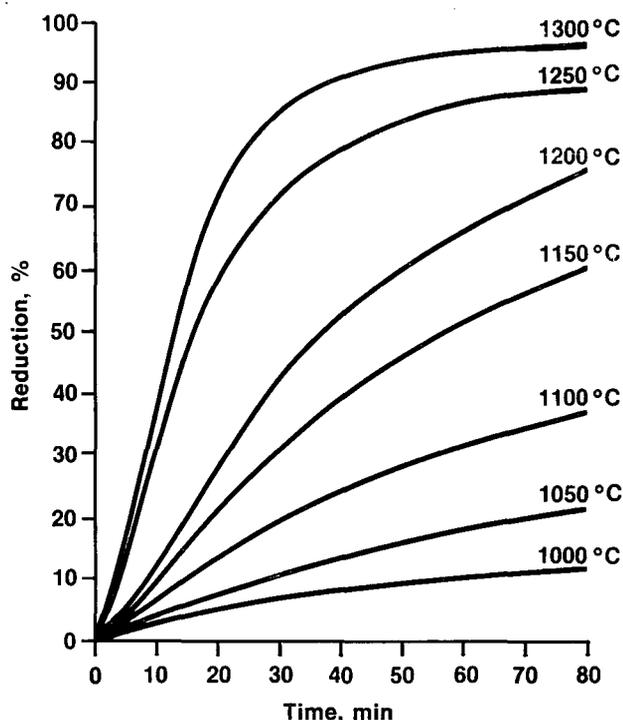
Fig. 1—Reduction versus time for pellets of CW chromite at various temperatures
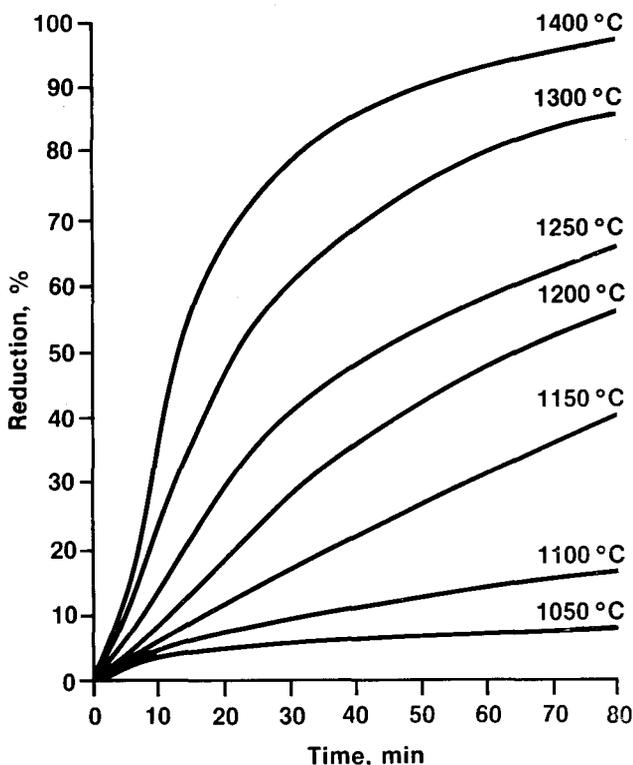

Fig. 2—Reduction versus time for pellets of CP chromite at various temperatures

reduction than CP ore at all temperatures, the difference being more marked at low temperature.

Gas Analyses

An analysis of the gases exiting from the furnace showed that carbon monoxide is the product of the reaction. The rate of gas evolution corresponded to the rate of mass loss. Small quantities of carbon dioxide were also detected. These quantities were slightly larger than that predicted by the thermodynamics of the Boudouard reaction ($C + CO_2 = 2CO$). These results did not indicate any particular reaction mechanism, but confirmed that the measurement of mass loss is a sound basis for reduction calculations.

Reproducibility of Results

The chromium and iron balances calculated for the reduced ores showed some variation in the composition of the green pellets. A larger quantity of pellets than those previously manufactured were made by use of a disc pelletizer instead of by hand rolling. Eight samples of these pellets, prereduced under conditions identical to the conditions for the earlier pellets, gave excellent reproducibility, and showed that the largest errors result from inadequate blending.

Comparison between CW Ore and Winterveld Ore

In a comparison of the reducibility of UG-2 ore with that of a typical Transvaal ore, pellets of Winterveld ore (WV) were reduced under conditions identical to those used for CW ore. CW ore showed a higher rate of reduction under the test conditions (1250°C under argon).

Smelting Results

Composition of the Slag

A large amount of data is available concerning the physicochemical properties of typical slags produced during the smelting of ferrochromium alloys.

A series of nine smelting tests[5] was carried out on fines (85 per cent of the particles smaller than 150 μm) from the two UG-2 ores to show the effect of slag composition on recovery of chromium and grade of alloy produced. The smelting of CP ore produced alloys with a chromium content of more than 51 per cent at an average relative chromium recovery of 92,2 per cent. The slags analysed 4 per cent Cr_2O_3, 0,5 per cent FeO, 41 per cent SiO_2, 2 per cent CaO, 18 per cent MgO, and 31 per cent Al_2O_3. CW ore, which has a slightly lower chromium-to-iron ratio, yielded alloy grades between 47,1 and 51,7 per cent chromium, with an average of 49,3 per cent. The carbon contents averaged 8,3 per cent, and silicon 0,6 per cent. The chromium recovery was 92 per cent. Although the compositions of the slag in the smelting of CW ore varied widely, the grade of alloy and the recovery of chromium apparently varied independently of the slag properties.

The results of these experiments indicate that the composition of the slag can be selected on the basis of liquidus temperature, viscosity, and resistivity, and that attempts to alter the composition of the alloy by an adjustment of the slag chemistry would meet with little success.

It was thought that a minimum slag-to-metal ratio could be achieved at the same time as a slag having the desired properties. Flux additions of 15 to 20 per cent quartz and 8 to 12 per cent burnt dolomite produced slag compositions of 34 to 40 per cent SiO_2, 6 to 10 per cent CaO, 24 to 28 per cent MgO, and 26 to 32 per cent Al_2O_3 (on a chromium-free and iron-free basis).

ANALYSES OF ALLOYS AND SLAGS FROM COMPARATIVE SMELTING
TESTS OF PREREDUCED AND UNREDUCED CHARGES AFTER 20
MINUTES AT 1680 °C

Alloy	Cr	Fe	Si	C	Total
CW (unreduced)	47,0	37,0	6,76	7,0	97,76
CW (prereduced)	49,0	38,7	3,68	8,0	99,38
WV (unreduced)	52,1	34,4	2,70	8,6	97,80
WV (prereduced)	49,3	37,1	4,58	7,6	98,58

Slag	Cr_2O_3	FeO	SiO_2	CaO	MgO	Al_2O_3	Total
CW (unreduced)	3,45	1,90	29,7	15,75	20,4	29,7	100,90
CW (prereduced)	0,68	<0,5	27,9	11,2	26,0	33,6	99,88
WV (unreduced)	4,28	2,28	35,1	4,98	24,7	30,3	101,64
WV (prereduced)	7,5	2,9	21,1	8,9	27,3	32,1	99,80

Comparative Smelting Tests

In a comparison of the behaviour of different ores during smelting, the following technique was used. The empty furnace was brought to temperature (1680 °C), and the charge was added without alteration of the power to the furnace. After 20 minutes at the desired temperature of 1680 °C, samples of slag and metal were taken. After 40 minutes, the furnace was tapped and all the samples and products were prepared for analysis. Four charges were tested: unreduced CW ore, prereduced CW pellets, unreduced WV ore, and prereduced WV pellets.

The analyses of the samples taken after 20 minutes are given in Table I, which shows that there were no significant differences between the prereduced charges and the normal charges. The reduction of the chromium and iron was nearly complete by the time the furnace had reached the required temperature (1680 °C), and the slag was completely fluid after 20 minutes. Further heating merely caused an increase in the silicon content of the alloys (Fig. 3) without a significant improvement in the recovery of chromium and iron.

Energy Requirements for Smelting

A computer program that had been developed to calculate the energy requirements in the smelting of chromite ores to ferrochromium, and that had been successfully applied to operating furnaces[8], was used to

calculate the energy requirements in the smelting of UG-2 ore. For ease of comparison, energy balances for Winterveld ores were also calculated with the aim of achieving identical slag compositions. Table II shows the energy requirements needed for each of the two ores in the production of 1 t of liquid high-carbon ferrochromium without preheating or prereduction of the ores.

Fig. 4 shows the effects on the power requirements in the preheating of unreduced and prereduced ores. For the UG-2 ore prereduced at 1250 °C and preheated to 800 °C, the power required was less than 1,5 MW·h per ton of alloy produced. On the basis of the contained chromium, the power requirements for UG-2 ores are lower than for Winterveld ore under all conditions.

Discussion and Results

Reducibility of Ores

Slatter[9] attempted to combine some of the chemical parameters of Zimbabwean chromites in evaluating their suitability for the production of high-grade (more than 65 per cent chromium) high-carbon ferrochromium.

Certain of these parameters are applicable to reducibility, i.e. the ratios of chromium to iron and of refractory to non-refractory. The latter (R:non-R) is defined as follows:

TABLE II

HEAT REQUIREMENTS FOR THE SMELTING OF HIGH-CARBON FERROCHROMIUM WITHOUT PREHEATING
OR PREREDUCTION OF PELLETS

Heat required	CW pellets		WV pellets	
	$MJ·t^{-1}$	%	$MJ·t^{-1}$	%
Heating of ores	3 927	35	4 079	32
Heating of fluxes and reducing agents	1 643	15	1 898	15
Reduction reactions	4 226	38	5 407	42
Fusion of metal	437	4	532	4
Fusion of slag	1 235	11	1 239	10
Super-heating of metal	22	0,2	24	0,2
Super-heating of slag	149	1	145	1
Sensible heat in gas (credit)	−462	−4	−547	−4
Total	11 178	100	12 772	100
Alloy, $kWh·t^{-1}$	3 516		4 018	

Unreduced

☐ WV
⊙ CW

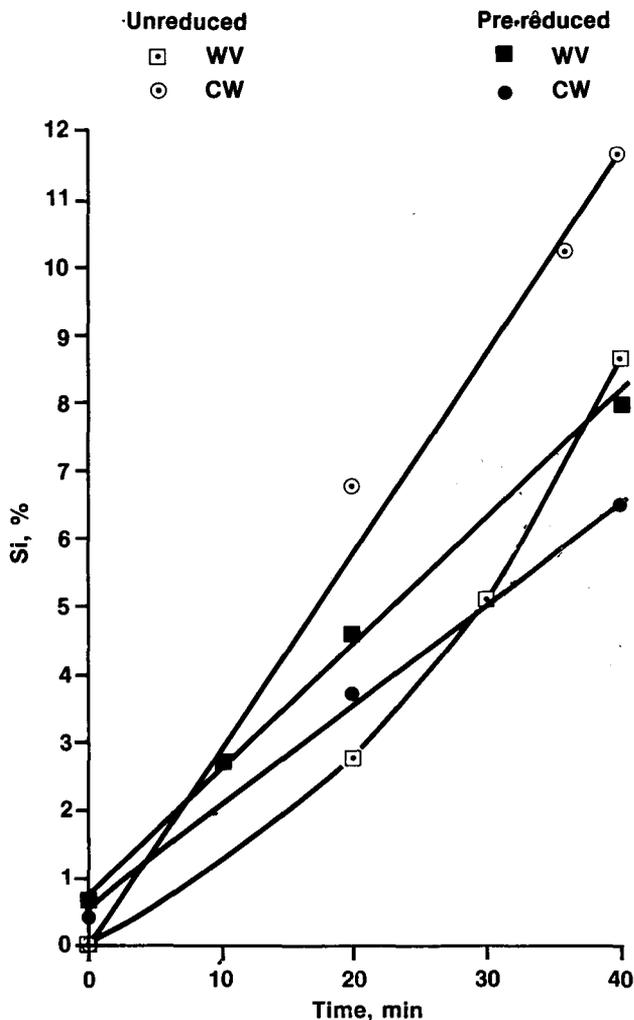**Pre-reduced**

■ WV
● CW

Fig. 3—Silicon in the alloy formed by smelting at 1680 °C as a function of time

$$R : \text{non-R} \quad = \frac{\text{Cr}_2\text{O}_3 + \text{MgO} + \text{Al}_2\text{O}_3}{\text{FeO} + \text{Fe}_2\text{O}_3 + \text{SiO}_2} \ .$$

Slatter[9] states that, all other factors being equal, R: non-R provides the best general measure of reducibility (an ore with a low ratio being more reducible than one with a higher ratio).

On this basis, the CW ore has a reducibility rating of 95 per cent and WV ore a rating of 85 per cent, the average of all the South African ores tested being 66 per cent[9]. The rating therefore confirms the experimental observation that CW ore is more reducible than the highly reducible Winterveld ore, and provides a quick estimate of relative reducibility.

The Kinetics of the Reduction

Sohn and Wadsworth[10] have systematically described the relationship between conversion and time for an isothermal first-order reaction of a non-porous solid with a fluid.

Microscopic examination of reduced chromite pellets shows that their size does not change during reduction, and that reduction occurs on their surfaces. This permits the adoption of a shape factor[10] of 1 (an infinite plane)

and, in the absence of external mass transfer, the general equation reduces to

$$ckt = X + \sigma_s^2 X^2,$$

where X is the fractional conversion, $\sigma_s^2 = \dfrac{k \cdot r}{2D_e}$,

and where r is particle radius,

  D_e is effective diffusivity, and

  k is a rate constant.

From the thermogravimetric curves and chemical analyses, the degree of iron metallization versus time can be obtained for each temperature tested after a correction has been made for the $Fe^{3+} \rightarrow Fe^{2+}$ reaction.

As is apparent from Fig. 5, the plot of X versus t is linear. Although this is a prerequisite for chemical control, Sohn and Wadsworth[10] have shown that this is possible even with σ_s^2 values as large as 0,5, indicating mixed control. Thus, the possibility of mixed chemical and diffusion control cannot be excluded in the absence of the diffusivity data required for the evaluation of σ_s^2.

From the Arrhenius equation

$$k \quad = k_0 e^{-E/RT} \qquad \text{and}$$

since $X = kt$ or $k \propto \left(\dfrac{dX}{dt}\right)_{t \to 0},$

values of k_0 and E (the activation energy) can be obtained from a plot of $\ln k$ against the inverse of the absolute temperature $(1/T)$. The values of
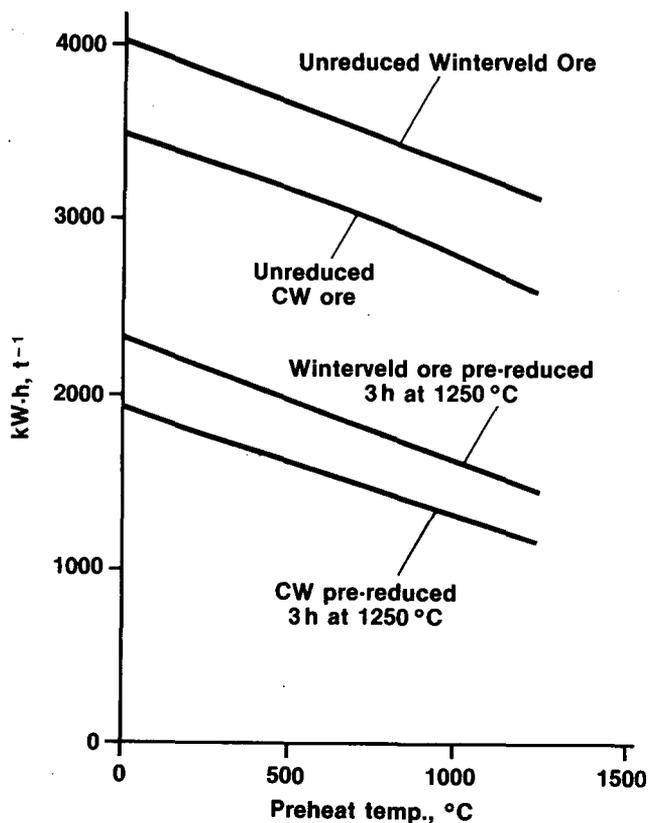

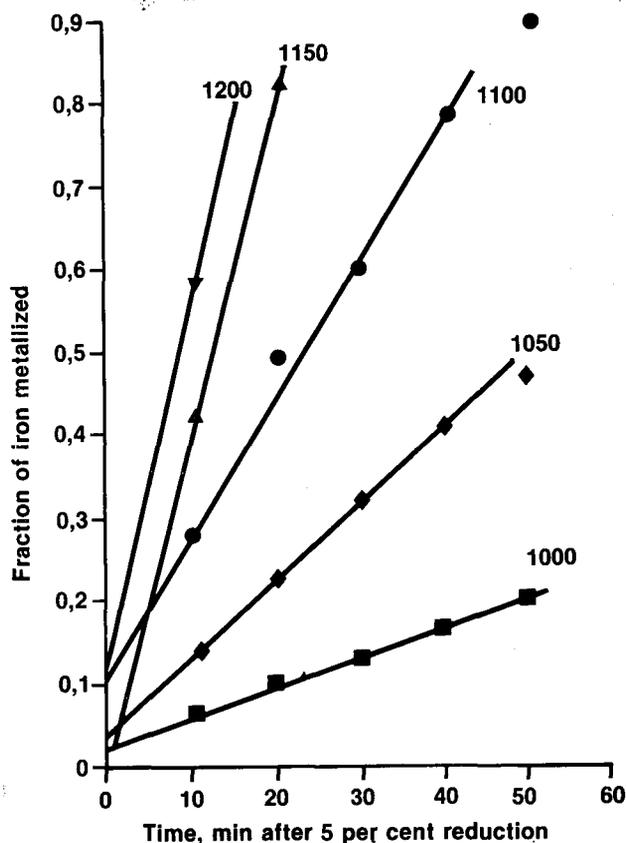Fig. 4—Power required for the preheating of unreduced and prereduced pellets

Fig. 5—Fractional iron metallization versus time for CW pellets

k_0 and E for CW ore are 15,93 min^{-1} and 181 kJ mol^{-1}.

As the values obtained are typical of a wide variety of reaction mechanisms, no firm conclusion can be drawn concerning the rate-controlling mechanisms, and the values for k_0 and E are useful only in the interpolation of the reduction rates for temperatures not used in this study, and possibly in the estimation of the time required at a given temperature before chromium starts to metallize.

Economic Considerations

Although UG-2 ore has certain technical advantages and disadvantages, its exploitation for the production of ferrochromium will ultimately depend on economic factors.

The gravity concentrate that is produced from UG-2 ore after the PGM have been removed contains more than 50 per cent chromium and iron. However, under present marketing conditions, iron has no resale value to producers of ferrochromium. While a surplus situation exists, the pricing system is unlikely to change. The fineness of the ore makes transportation and handling difficult, and means that agglomeration by the producer is desirable.

The high reducibility of the ore and the high degree of prereduction that can be obtained in the solid state favour the application of a smelting route involving a prereduction step. Such a process requires high capital investment in an expensive plant. On the other hand, the fact that the costs of mining and milling have been borne by the PGM operation should allow a greater degree of

flexibility in the pricing of the ore, which could affect the ferrochromium industry significantly.

Conclusions

(1) UG-2 ore is highly reducible, and substantial prereduction in the solid state is feasible.

(2) Whereas an alloy containing 50 per cent chromium may be produced successfully, there is no difficulty in the production of a high-carbon ferrochromium alloy containing 48 to 50 per cent chromium. The acceptability of this alloy will depend on economic conditions.

(3) Theoretical calculations show that the processing of UG-2 chromites yields significant savings in the total energy and electrical power required, both per unit of ferrochromium produced and per unit of chromium content.

(4) More than 50 per cent of the energy requirements can be met outside the smelting furnace.

(5) The fluxing requirements of UG-2 ores are such that the material can be smelted under conditions very similar to those normally used for other Transvaal chromites.

(6) No particular problems are encountered in the smelting of prereduced UG-2 concentrates.

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