THE PRODUCTION OF FERROCHROMIUM

IN A TRANSFERRED-ARC PLASMA FURNACE

by

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Introduction

Recent developments in the production of high-carbon ferrochromium have centered on the conventional submerged-arc electric smelting furnace in which chromium ore is reduced carbothermically.

Major improvements made include increased furnace size and megavoltampere rating, the utilization of chromium-ore fines via agglomeration techniques, e.g., pelletizing and briquetting, and the pre-treatment of agglomerated chromium ores, e.g., pre-heating and pre-reduction (1,2). Computerized control of this smelting process has helped to increase productivity still further (3).

The immediate future of this industry depends on optimization of the existing production method to minimize costs. Equally important, however, is the development of new, more flexible processes that can utilize cheaper lower-grade raw materials, e.g., unagglomerated ores and fine coals, in a highly efficient manner.

Plasma technology has the potential to realize this latter objective and, in South Africa, the Council for Mineral Technology (Mintek) - formerly the National Institute for Metallurgy (NIM) -has maintained a watching brief for several years on plasma developments world wide (4).

Even though the submerged-arc furnace route is by and large a tried and tested method, it does have some noteworthy disadvantages, as follows.

1. If good metallurgical performance is to be achieved, the feed materials must be carefully sized and invariably screened and agglomerated before being fed to the furnace.

2. The electrical conductivity of the carbonaceous reducing agent and the slag often limit the power input to the process.

3. The lack of direct control over the rate at which the feed material descends into the hot reaction zone prevents effective regulation of the temperature of the process. For example, the poor recoveries obtained from Transvaal chromites are probably due to this lack of control. The losses occur mostly in the form of undissolved chromium-ore spinel (5).

4. The large volume of unreacted burden in the furnace necessitates the use of a much larger reaction vessel than would otherwise be needed.

5. Owing to the long time constants required for the process, feedback control is somewhat ineffective, and overshoot-undershoot phenomena are a regular feature of the operation.

6. The self-baking electrodes often give problems, e.g., long delays due to breakages. Also, electrodes are a costly consumable item.

The Potential Advantages of Plasma Technology

Several benefits are to be derived from plasma technology, among which are the following.

a. A major potential benefit of some thermal plasma systems is their ability to treat fines direct, i.e., without costly prior agglomeration.

b. A second important advantage is the flexibility of certain thermal plasma processes with respect to the choice of carbonaceous reducing agents for smelting. Cheap, finely sized coals containing high proportions of ash and volatile materials can be used instead of the considerably more costly cokes and chars required for the conventional

process.

c. A third advantage of plasma technology over the submerged-arc furnace process is the extra degree of freedom permitted, in that the feed rate of the raw materials and the power input can be directly controlled to maintain steady-state conditions.

d. Water-cooled plasma electrodes are used instead of costly graphite electrodes, which results in a considerable saving. Such devices can form very stable plasma arcs.

Development of Plasma Systems

A great many different plasma systems were developed over the past two decades, many of which have been used in the study of pyrometallurgical applications (6). Much of the earlier work was conducted in bench-scale tests, but, more recently, several pilot plants were built on a semi-industrial scale, and there are even some full-scale facilities (7-9).

The most widely accepted classification of plasma systems as applied to pyrometallurgical processes is as follows.

(1) Transferred-arc plasma is that in which a direct-current arc is transferred from a water-cooled cathode (the plasma gun) to the anode, which is normally the bath. An example of this system is the Expanded Precessive Plasma of Tetronics Research and Development Limited (TRD), which was developed in association with Foster Wheeler Energy Limited (10).

(2) Non-transferred-arc plasma is that in which the arc (either alternating or direct current) is struck between two counter electrodes, normally two water-cooled annular rings. A "tail flame" of plasma projects beyond the so-called downstream electrode and impinges on the material being processed as the reactants are injected into the tail flame. An example of this device is the Westinghouse Arc Heater (8).

Middelburg Steel and Alloys (MS&A) identified the potential benefits of plasma several

years ago and, with Mintek, undertook a ser trials on the plasma-arc facility at TRD. facility was selected by MS&A and Mintek as a suitable pilot plant on which to conduct lurgical trials and to investigate the pot benefits of plasma for the smelting of high carbon ferrochromium from Transvaal chromiu fines and fine carbonaceous reducing agents especially cheap coal with high contents of and volatile materials.

To achieve these objectives, the inves tors preferred the method in which the reac take place in a liquid bath rather than the ternative method of so-called "in-flight" reactions.

Experimental Method

The overall layout of the test facilit at TRD is depicted in Figure 1, and althoug several preliminary tests were carried out 300 kVA plasma furnace, the following descr is of the more significant testwork done on 1.4 MVA furnace.

----→ Signals to and from PLC
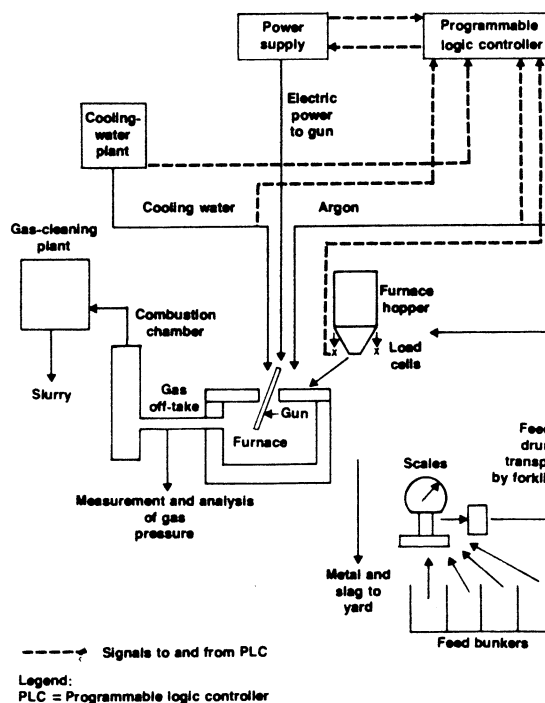
Legend:
PLC = Programmable logic controller

Figure 1. General plant lay-out at Tetroni Research and Development Limited

Raw Materials

The chemical composition and the range of the mean particle size for each of the raw materials used is given in Table I. The chromite came from the Winterveld mine, and the coal from the Springbok no. 5 seam, both in the Transvaal. Rand Carbide Limited supplied the char, and TRD the quartz and lime fluxes. All suppliers sent dry materials, primarily to ensure constant feed compositions and consistent behaviour in the feed system.

The various feed compositions used (Table II) were prepared as follows. The raw materials were weighed out into 50 kg batches, mixed for 5 minutes in a small concrete mixer, placed in 200 kg batches in drums, and transported to the feed hopper of the furnace. The various feed mixtures were varied primarily according to the proportion and type of reducing agent, but two changes were made to the flux additions as well. A slag with composition of 12 per cent Cr_2O_3, 6 per cent FeO, 35 per cent SiO_2, 0.35 per cent CaO, 19.3 per cent MgO, and 27.4 per cent Al_2O_3, which would have a liquidus temperature of approximately 1640°C and a viscosity of 0.3 to 0.8 Pa·s, was the basis for the initial flux addition required. The changes made to the initial flux addition during the trials are described in the discussion. Those changes in the type and proportion of reducing agent used were largely governed by the stability of the plasma arc in any particular furnace environment.

Table I - Chemical analyses and sizing of the raw materials

Raw material	Composition, mass %					
	Cr_2O_3	FeO	SiO_2	CaO	MgO	Al_2O_3
Chromium Ore:						
Winterveld chromite $0.1 < \overline{d} < 2.0$ mm	44.6	23.3	2.23	0.20	11.2	13.1
Fluxes:						
Quartz $0.1 < \overline{d} < 0.7$ mm	-	0.20	99.5	-	-	0.0
Lime $0.01 < \overline{d} < 0.08$ mm	-	0.04	0.05	95.0	0.20	-

Carbonaceous Reducing Agents:	Fixed carbon	Volatile material	SiO_2	Al_2O_3	S	P
Finely sized coal $0.4 < \overline{d} < 2.0$ mm	54.3	33.4	7.5	2.5	0.63	0.004
Larger sized coal $4.0 < \overline{d} < 10.0$ mm	51.4	36.7	8.50	5.40	0.64	<0.005
Finely sized char $0.6 < \overline{d} < 0.7$ mm	79.0	4.11	11.10	3.0	0.39	0.021

$\overline{d}$ = mean particle size, mm

< = less than

Table II - Feed compositions

Recipe designation *	Composition, mass % of the ore					
	Winterveld ore	Quartz	Lime	Coal <2mm	Coal <10mm	Ch <2
S1/2	100.0	18.0	-	-	-	25
S1/5	100.0	19.0	-	35.0	-	
S1/7	100.0	19.0	-	50.0	-	
S1/8	100.0	19.0	-	-	50.0	
S2/1	100.0	25.0	-	-	-	
S3/1	100.0	20.0	5.0	10.0	-	20
S3/2	100.0	20.0	5.0	-	40.0	

* S = Smelting recipe (S1 = Standard recipe)

(S2 = Additional quartz)

(S3 = Lime addition)

The Plasma System

The various components of the overall plasma system (Figure 1) that were of particular importance in evaluation of the trials are discussed below.

The Furnace. Figure 2 is a drawing of the 1.4 MVA plasma furnace, which depicts the major features of its design. These were changed substantially only once during the trials when the height of the side walls was increased by 0.23 m to that shown in Figure 2. A single exhaust port was used to convey the off-gas direct from the furnace into a horizontal combustion chamber. Three feed ports spaced at equal intervals round the central plasma-gun emplacement were used to drop feed under gravity into the circle defined by the anode root of the precessing plasma gun. The furnace was tilted hydraulically for removal of the liquid metal and slag, which were cast into large refractory-lined metal trays. The roof of the furnace was used to support the plasma gun and its accompanying service manifold as well as the entire feed system. A steel anode, of which the external connection below the fur-

nace had fins, was used to maintain electri contact with the internal molten bath.

Plasma Gun. In all essentials, the pl gun, which is schematically depicted in Fig was as described in the patent literature (and was mounted as shown in that Figure. 1 precessed by a hydraulic motor at approxima 50 r/min at an angle of 9° from the vertica Electrical current was supplied by a water-cooled lead from the services manifold to t plasma-gun cathode at up to 1250 A (briefly 1450 A). Argon gas from a bulk liquid stor tank was supplied at 3 to 4 Nm³/h, and de-i (0.5 mS/m) cooling water at a pressure of 6 700 kPa was used to remove between 20 and 3 of heat from the gun at a flowrate of betwe and 3.5 m³/h with a maximum permissible out temperature of 55°C. A series of gun lengt between 380 and 500 mm were used during the trials, which yielded arc lengths of from 5 350 mm within the furnace.

Power Supply. A simplified drawing of power supply is given in Figure 4. The ste down transformer had two secondary windings
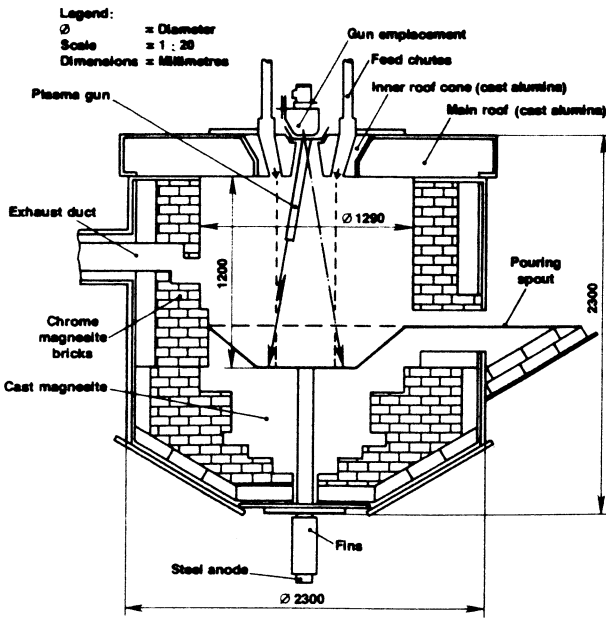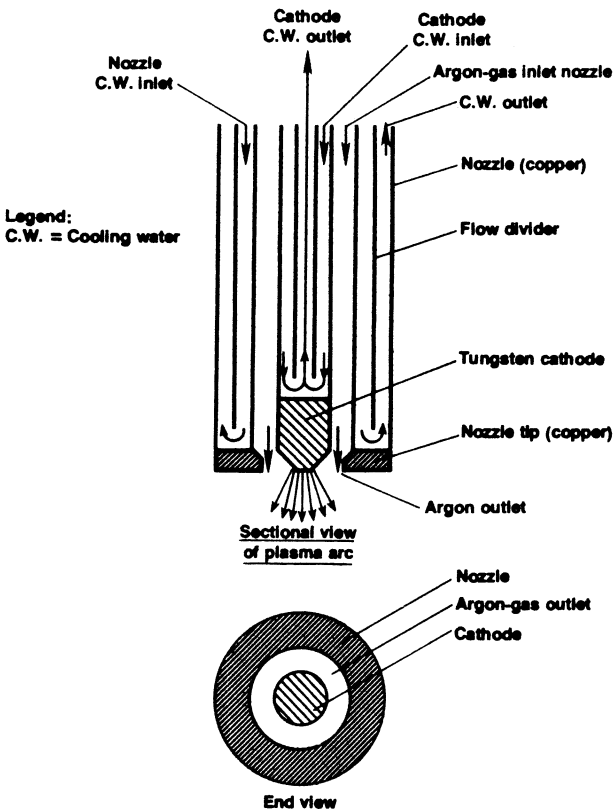
Figure 2. Arrangement of a 1400 kVA furnace
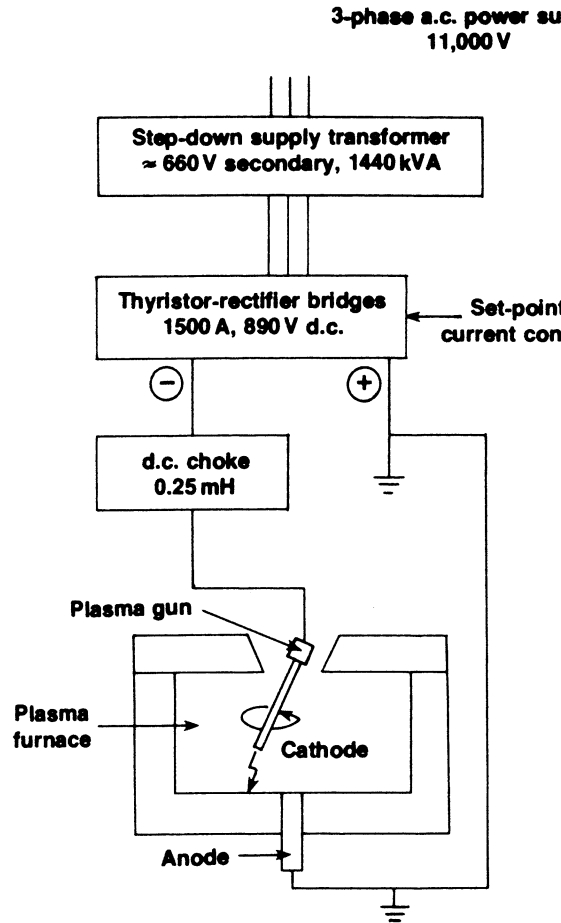

Figure 3. Schematic representation of the plasma gun

Figure 4. Simplified representation of the power supply

produce a phase shift of 30° between the outpu
which provided a suitable supply for a twelve-
pulse thyristor-based rectifier. The thyristo
were controlled by a constant-current circuit
that formed the primary control of the power i
put to the process, whereas the overall resist
vity of the arc itself had the largest process
dependent effect upon the maximum power input.
series of interlocks that were automatically a
vated by a programmable logic controller (PLC)
whenever any detectable malfunction (e.g., in
supply of argon gas) occurred, formed the back
ground control function for the power supply a
the plasma gun. The logic controller also car
out the sequential operations required to star
up the plasma gun.

Auxiliaries. A table feeder was used wit
three "ploughs" that displaced material from t

TABLE III

Metallurgical results

| Recipe no. | Total | Input feed, kg | | | | | Tap no. | Output kg | | Analysis of output, % | | | | | | | | | | | Thermodynam energy consumption* kW·h/t |
| | | Ore | Quartz | Lime | Coal | Char | | | | Slag | | | | | | Metal | | | | | |
								Slag	Metal	Cr₂O₃	FeO	SiO₂	CaO	MgO	Al₂O₃	Cr	Fe	Si	C	S	
S1/2	80.0	55.9	10.1	–	–	14.0	1	24	30	2.5	1.8	35.7	1.5	29.1	30.2	54.8	33.0	4.9	6.0	0.02	3131
S1/5	90.1	58.5	11.1	–	20.5	–	1	31	27	14.4	1.9	35.5	0.6	22.3	24.8	55.1	37.6	0.3	5.7	0.10	3114
S1/5	340.1	220.8	42.0	–	77.3	–	2	126	93	19.5	3.1	33.5	0.5	19.8	23.8	53.9	39.2	0.5	5.5	–	3259
S1/5	120.0	77.9	14.8	–	27.3	–	3	44	33	21.1	2.3	33.2	0.4	19.8	23.9	53.1	40.5	0.6	5.3	0.10	3282
S1/5	375.0	243.5	46.3	–	85.2	–	4	140	101	22.2	1.7	33.2	0.5	19.2	24.0	52.2	41.4	0.4	5.4	0.08	3271
S1/5	355.0	230.5	43.8	–	80.7	–	5	133	94	21.4	2.7	32.7	0.5	18.7	24.2	53.6	40.9	0.4	5.2	0.10	3325
S1/5	380.1	246.8	46.9	–	86.4	–	6	145	101	22.2	2.7	33.4	0.4	18.2	24.1	52.3	40.7	0.5	5.2	0.08	3302
S1/5	350.1	227.3	43.2	–	79.6	–	7	138	90	23.3	3.6	32.8	0.4	18.2	22.7	52.3	41.0	0.4	5.5	0.08	3368
S2/1	647.0	417.0	104.0	–	–	126.0	1	179	230	4.1	2.0	35.2	0.9	23.1	34.4	53.0	31.4	7.8	5.6	0.02	3316
S2/1	646.0	416.0	104.0	–	–	126.0	2	177	229	4.9	1.7	34.7	1.0	24.0	33.9	52.5	31.6	8.3	5.6	0.07	3337
S1/7 } S1/8 }	620.0	372.0	70.0	–	178.0	–	1	160	197	3.9	1.1	31.7	0.9	27.8	33.7	55.3	33.5	3.7	5.7	0.04	3174
S3/2	180.0	109.0	22.0	5.0	44.0	–	1	52	58	2.9	0.7	31.6	3.0	28.5	32.6	55.7	33.7	3.6	5.4	0.04	3194
A	856.0	535.0	113.0	17.0	118.0	73.0	1	277	267	6.3	2.1	34.1	3.8	29.6	22.2	56.3	34.3	1.1	6.8	–	3150
S3/2	577.0	350.0	70.0	17.0	140.0	–	1	184	181	3.2	0.9	35.0	5.4	26.1	27.1	56.5	34.2	1.3	5.4	0.08	3108

* The minimum energy required per ton of metal calculated from standard thermodynamic data
A = Four recipes combined: S3/2, S2/1, S1/8, and S3/1

rotating table into the sealed feed tubes, which were also purged with argon. A central cone was used to distribute the feed from the hopper evenly upon the rotating table. The entire feed assembly was suspended from load cells that provided a digital display of the mass of the feed hopper. The rate at which mass was lost from this feeder gave an immediate measurement of the feed rate, without the need for a calibration test for each material.

The off-gas system employed a wet-spray scrubber and demister, followed by a centrifugal fan and stack, to dispose of the hot, combusted furnace gas. The quantity of excess air drawn into the combustion chamber was used to control the furnace pressure, and an on-line gas analyser (CO, CO_2, and O_2) served to monitor the furnace atmosphere. There were several thermocouples installed at various points in the furnace refractories, the outputs of which were monitored and recorded. An infrared pyrometer was installed on the side wall of the furnace shell. This instrument monitored the changes in the surface temperature of the melt via a sighting tube through the refractories, which was purged with argon. All the flows and temperatures of the services to the plasma gun were monitored, as well as power and energy inputs, operating voltages and currents, the mass of the feed hopper, gas analyses, and the output of the infrared pyrometer.

Furnace Operation

The furnace was pre-heated, by use of a graphite electrode, to an internal temperatur approximately 1100°C, at which stage the plas

Legend:
Based on 3280 kW·h per ton of metal
Feed/metal ratio = 3.1:1
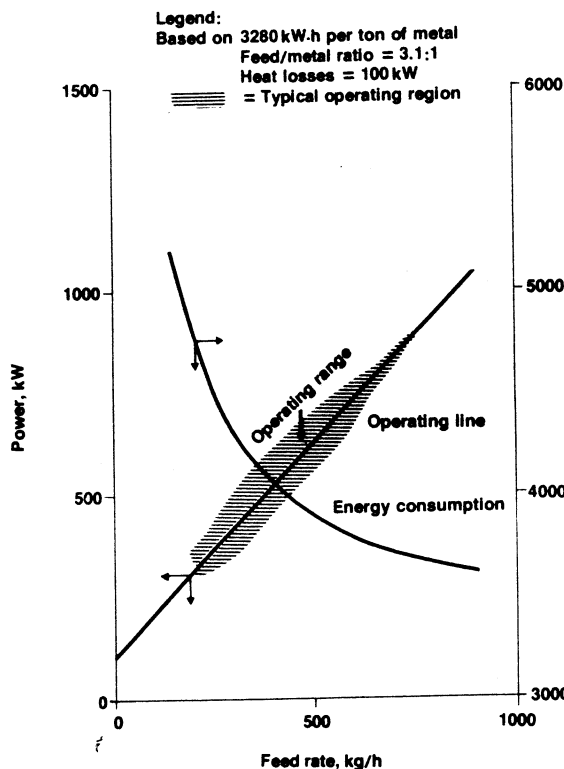Heat losses = 100 kW
═══ = Typical operating region

Figure 5. Calculated graphs for energy consumption and operation showing normal operating range during the plasma trials

gun was installed. A high-frequency voltage was then used to provide an initial conductive path from the plasma-gun cathode to the surrounding nozzle that had been temporarily connected as an anode. A graphite rod was then used for manual transfer of the arc from the cathode to the hearth that provided the current with a return path having the lowest resistance.

The established plasma arc was used to raise the furnace temperature to approximately 1700°C, and then to attain steady-state conditions. The graphite electrode was used to maintain constant temperatures overnight and between planned test runs.

The primary aim in operation of the furnace was the maintenance of a constant temperature throughout the run. This necessitated a balance between the feed rate and the power input, a relation that is illustrated in Figure 5. The slope of the operating line was calculated from the energy required (from thermodynamic data) to process one kilogram of feed (Table III). The intercept was the sum of the heat losses from the furnace and from the plasma gun, which were determined from the power input required overnight (approximately 70 kW), and the measured heat gain from the cooling water (approximately 30 kW) respectively. Accordingly, the furnace was run as close to the calculated operating line as possible but, in addition, the changes in the thermocouple outputs and the readings from the infrared pyrometer were taken into account because of the known limitations of the calculated operating line.

The furnace pressure was kept slightly positive (0.40 kPa) and the carbon monoxide content of the off-gases was kept as high as possible. The slag and the metal were tapped intermittently. No feed was added during tapping, although the plasma gun was left on at a suitably reduced power.

<div align="center">

Results

</div>

The results of the plasma trials are discussed under two headings, namely, metallurgical and operational results. Although four separate campaigns were conducted, two on the 300 kVA and two on the 1400 kVA facilities, only the most relevant results are presented here to highlight the successes and the failures of the plasma tests.

Operational Results

The primary aim of the campaign was essentially the attainment of good metallurgical performance, and the operational results are therefore not directly representative of the actual capabilities of the system. However, one experimental run had, as its objective, the attainment of good operational results and the attainment of steady-state conditions with a single feed composition. A maximum plasma-gun current well within the capabilities of the gun was selected, and an arc length chosen that would yield stable operation. This run therefore provided a controlled test of the operation of the system. The detailed data for the power and feed rate from the run are presented in Figure 6, and the hearth temperatures measured during the run are shown in Figure 7. The slag and the metal were tapped easily from the furnace during this run, but exact control of the tilting angle was difficult, and, as a
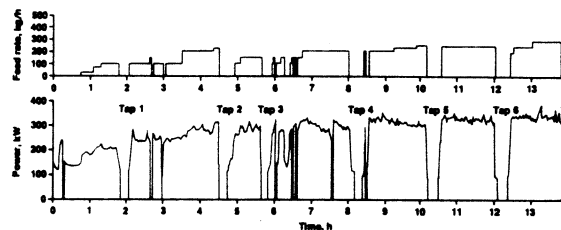

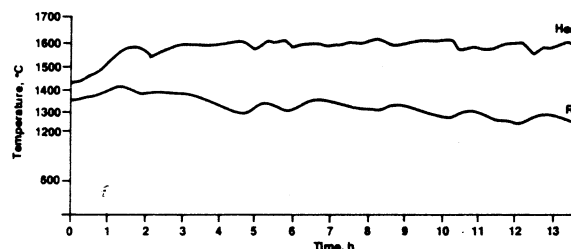
Figure 6. Power and feed rate during a steady run

Figure 7. Hearth and roof temperatures during a steady run

TABLE IV

SMELTING BALANCE

	KG	CR2O3	FEO	SIO2	CAO	MGO	AL2O3	CR	FE	SI
CHROMITE	227.30	44.60	23.30	2.23	.20	11.20	13.70			
QUARTZ	43.20	0.00	.20	99.45	0.00	0.00	.06			
COAL FINES	79.60	0.00	0.00	7.50	0.00	0.00	2.50			
TOTAL		101.38	53.05	54.00	.45	25.46	33.16			
TOTAL & FINES		101.38	53.05	54.00	.45	25.46	33.16	0.00	0.00	0.00
TO METAL		68.73	47.51	6.92	0.00	0.00	0.00	47.01	36.92	3.24
TO SLAG		32.17	4.97	45.28	.44	24.08	32.49			
SMOKE LOSS		.48	.56	1.79	.01	1.37	.66			
ANALYSIS(SLAG)		23.30	3.60	32.80	.40	18.20	22.70			
ANALYSIS(METAL)								52.26	41.04	.40

EXCESS CARBON = 45.92 %

RECOVERIES AS %

	CHROME	IRON	SILICON
FROM ORE	67.80	89.57	1.40

SLAG FORMING RATIOS

MGO/SIO2 : .55
MGO/CAO : 45.50
MGO/AL2O3 : .80

CR/FE RATIO (ORE): 1.68
SLAG/ALLOY RATIO : 1.53

MASS (KG) OF:
SLAG = 138.06
ALLOY = 89.96

SLAG LIQUIDUS TEMPERATURE = 1549. DEG C
METAL LIQUIDUS TEMPERATURE = 1545. DEG C
SLAG CONDUCTIVITY = 18.957 SEIMENS/M

VISCOSITY = .710 N.S/M**2 (7.095 POISE)

HEAT BALANCE TABLE (BASED ON THE PRODUCTION OF ONE METRIC TON OF CHARGE CHROME)

HEAT PROVIDED FOR:	KJOULES	K.W.H.	TEMPERATURES K		
HEATING OF RAW MATERIALS	6198770.00		FROM	298.00 TO	1950.00
REDUCTION REACTIONS	4622638.00				
FUSION OF METAL	474553.31				
FUSION OF SLAG	1058495.00				
HEAT INPUT	12354456.00	3430.83			
OFF-GAS HEAT LIBERATED	225355.81	62.58	FROM	1950.00 TO	1473.00
THERMODYNAMIC REQUIREMENT	12129100.00	3368.25			

result, direct comparison of the masses of the product with those calculated was unrealistic.

A complete chromium balance over the last twelve runs showed an error of 6.6 per cent, so that the reliability of the individual calculated mass balances was presumed to be of this order. The remaining operational parameters of significance are discussed in the section on operational performance.

Metallurgical Results

Table III gives a cross-section of typical results for the smelting of high-carbon ferrochromium in the transferred-arc facilities at TRD, as well as the code designating the recipe used for the raw materials, the quantity of material fed, and the composition and mass of the metal and the slag produced. The theoretical energy consumption that is thermodynamically attainable is

given in this table instead of the actual ene consumption, since this latter value is discus in the section on operational results. Typic: mass and energy balances for two of the tests presented in Tables IV and V. A computer pro: gramme was used to calculate these outputs.

Discussion

In terms of the operation of the plasma s tem and of the metallurgical behaviour of the process, the performance of the furnace can b evaluated by consideration of the representat: cross-section of results given in Tables III and Figures 5 and 6. The performance of the plasma system and especially the principles applied in the use of this equipment must be lated to the conventional method for the produ tion of ferrochromium in the submerged-arc fur nace if a realistic comparison is to be made.

TABLE V

SMELTING BALANCE

	KG	CR2O3	FEO	SIO2	CAO	MGO	AL2O3	CR	FE	SI	
CHROMITE	350.00	44.60	23.30	2.23	.20	11.20	13.70				
QUARTZ	70.00	0.00	.20	99.45	0.00	0.00	.06				
LIME	17.00	0.00	.04	.50	95.00	.20	0.00				
COAL	140.00	0.00	.30	8.50	0.00	0.00	5.40			.51	
TOTAL		156.10	82.12	89.40	16.85	39.23	55.55				71
TOTAL & FINES		156.10	82.12	89.40	16.85	39.23	55.55	0.00	0.00	0.00	71
TO METAL		149.47	79.59	21.90	0.00	0.00	0.00	102.24	61.84	10.24	9
TO SLAG		5.90	1.66	64.52	16.47	37.12	54.44				
SMOKE LOSS		.73	.87	2.96	.34	2.12	1.11				
ANALYSIS(SLAG)		3.20	.90	35.00	5.40	26.10	27.10				
ANALYSIS(METAL)								56.52	34.18	1.29	5

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EXCESS CARBON    =    18.56 %

RECOVERIES AS %
                 CHROME   IRON   SILICON
FROM ORE          95.75   96.92    5.59

SLAG LIQUIDUS TEMPERATURE  =    1650. DEG C
METAL LIQUIDUS TEMPERATURE =    1555. DEG C
SLAG CONDUCTIVITY = 47.309 SEIMENS/M
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SLAG FORMING RATIOS           MASS (KG) OF:
MGO/SIO2      :   .75         SLAG     =  184.35
MGO/CAO       :  4.83         ALLOY    =  184.90
MGO/AL2O3     :   .96

CR/FE RATIO (ORE):   1.67
SLAG/ALLOY RATIO :   1.02

VISCOSITY =    .162 N.S/M**2 ( 1.619 POISE)
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HEAT BALANCE TABLE (BASED ON THE PRODUCTION OF ONE METRIC TON OF CHARGE CHROME)

HEAT PROVIDED FOR:	KJOULES	K.W.H.	TEMPERATURES K
HEATING OF RAW MATERIALS	5091322.00		FROM 298.00 TO 1950.00
REDUCTION REACTIONS	4922152.00		
FUSION OF METAL	496311.13		
FUSION OF SLAG	912939.00		
HEAT INPUT	11422724.00	3172.09	
OFF-GAS HEAT LIBERATED	231644.00	64.33	FROM 1950.00 TO 1673.00
THERMODYNAMIC REQUIREMENT	11191080.00	3107.76	

Operational Performance

Only two major items of equipment required an evaluation of their operational performance, i.e., the plasma gun and the furnace itself, because all the auxiliary equipment was of standard design and function. The performances of the plasma gun and the furnace were considered in terms of reliability, efficiency, flexibility, and maintenance.

The plasma gun operated in one of two modes: (i) erratic unstable behaviour (i.e., large voltage "swings" and frequent water leaks due to stray arcs from the gun nozzle causing pitting and holing of the nozzle) and (ii) smooth, even, very controllable behaviour with no discernible wear in up to 20 hours of operation.

These two extremes are not well defined in terms of operational parameters (some of which

could be arc length, feed composition, and of gas removal) so that an empirical approach to specific situation appears to be the best bas for the achievement of good operation. The i cations obtained from the trial programme wer that an arc length of between 0.4 and 0.5 m a similar gun length would produce reliable ope tion with recipes S1/5 or S3/1 at a voltage o between 450 and 550 V. A typical gun heat lo defined as being the power loss to the coolin water as a percentage of the maximum power, w 5.5 per cent, which was largely due to heat losses through the relatively large surface a of the nozzle. Maintenance of the plasma gun not difficult because of its small size and r replacement (usually less than 30 minutes). replacement time could be improved upon if mo sophisticated handling equipment for the plas gun were installed on the furnace roof. The

flexibility of the plasma gun was also good, again largely because of the ease with which it could be replaced.

The reliability of the furnace was good in terms of the side walls, hearth, and anode, but poor with regard to the roof refractories. The use of a castable refractory and direct exposure to the radiation from the melt might have been responsible for this performance in view of the fact that bricks line the side walls. This behaviour of the roof refractory was largely responsible for the discrepancies in the mass balance of the slag in some of the runs. The heat loss from the furnace, measured as a fraction of the maximum power input, was 12.7 per cent (excluding the plasma gun). The overall efficiency of the smelting operation, as measured by the energy consumption per ton of metal product (in kilowatt-hours) could be determined with confidence only in the long run (Figure 6).

There was a difference of 13.1 per cent between the calculated and actual energy consumed during this run, which indicated that conventional thermodynamic data could be successfully used in the prediction of the performance of a plasma furnace. The relation between the overall feed rate and the calculated energy consumption at this scale of operation (including the heat losses) is shown in Figure 5.

A total of 13.8 t of feed material was processed during the trials to produce 5.2 t of high-carbon ferrochromium at powers of up to 750 kW. The flexibility of the furnace is potentially high because of the low inventory of materials, but is limited by the suitability of the refractories for various feed-stocks. The absence of a large burden of raw material makes rebuilding of the furnace quicker and simpler.

Metallurgical Performance

A computer programme to calculate the mass and heat balances for each of the smelting tests was of assistance in the evaluation of the metallurgical performance. This programme was used to give the output masses for the slag and

the metal (Table III), since it was not alway[s] possible for the furnace contents to be remov[ed] completely after each batch operation, as alr[eady] discussed above.

The first row of data in Table III shows that low values were obtained for chromium ox[ide] in a batch test on the smaller 300 kVA facili[ty] when 80 kg of feed produced 30 kg of metal an[d] 24 kg of slag containing only 2.5 per cent Cr_2O_3 and 1.8 per cent FeO.

The next seven rows give the results for [a] series of consecutive taps during an extended campaign of some 14 hours of operation of the 1400 kVA TRD plasma furnace. The recovery of chromium decreased dramatically with increasi[ng] feed rate, and hence the chromium oxide conte[nt] of the slag increased from 14.4 per cent at a feed rate of 200 kg/h to 23.3 per cent at a f[eed] rate of 350 kg/h.

The reason for the poor chromium recover[y] and therefore the high slag-to-metal ratio wa[s] thought to be related to a loss of carbonaceo[us] reducing agent - in this case the coal - by o[ne] or both of two possible mechanisms.

(1) Fine coal was entrained in the off-gas, a[nd] was removed from the furnace to be combus[ted] in the off-gas duct.

(2) The ingress of air, mainly via the feed system and exhaust duct, resulted in the combustion, in situ, of fine coal within [the] furnace.

A coarser coal fraction was selected in [an] attempt to overcome the first possible way i[n] which coal was lost, and the coal addition t[o the] feed was increased from 35 to 40 per cent.

The furnace was sealed more tightly, an[d] additional inert gas was used to purge the f[eed] system. The furnace was operated under slig[ht] positive pressure conditions to minimize the ingress of air, and a gas analyser was used [to] monitor CO, CO_2, and O_2.

Extra quartz flux was added to the feed [to] lower the liquidus temperature of the slag, [and] the silicon content of the metal increased s[lightly]

ly, as is shown in the ninth and tenth results in Table III. The quartz addition was decreased, and subsequently some lime was added to successfully lower the silicon content from 8.3 to 1.1 per cent. These actions resulted in slags that are low in chromium oxide, as shown in the last six rows in Table III.

Two typical examples of low and high recoveries are contained in printouts from the computer programme in Tables IV and V. Table IV illustrates a low chromium recovery of 67.8 per cent, a high slag-to-metal ratio of 1.53, and a relatively high "thermodynamic" energy consumption (Table III) of 3368 kW.h per ton of alloy. These

results are indicative of inadequate control o the smelting conditions. The very high recove of chromium of 95.75 per cent, the low slag-to metal ratio of 1.02, and the low "thermodynami energy consumption of 3108 kW.h per ton of met in Table V afford confirmation that, when cond tions are correctly controlled, favourable che stry is attainable in the smelting of chromium ore fines in a transferred-arc plasma system.

Possible Smelting Mechanisms

The chromium-ore fines, the fluxes (quartz, li and the carbonaceous reducing agent or agents (coal, char) were fed simultaneously into the

TABLE VI

Some of the reactions considered in the smelting of chromium ore in the plasma furnace at 1600°C

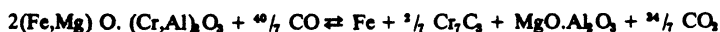Group I Control of the p_{o_2} in the gaseous phase

$C + \frac{1}{2}O_2 \rightleftarrows CO$

$C + O_2 \rightleftarrows CO_2$

$C + CO_2 \rightleftarrows 2CO$ (Bouduard reaction)

$CO + \frac{1}{2}O_2 \rightleftarrows CO_2$.
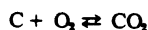
Group II. Solid state reductions on the surface of the bath. Iron oxide reduction becomes feasible at a p_{o_2} of less than 10^{-5} atm.

$(Fe,Mg) O. (Cr,Al)_2O_3 + CO \rightleftarrows \underline{Fe} + MgO. (Cr,Al)_2O_3 + CO_2$
or
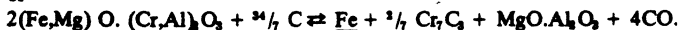$(Fe,Mg) O. (Cr,Al)_2O_3 + C \rightleftarrows \underline{Fe} + MgO. (Cr,Al)_2O_3 + CO$.
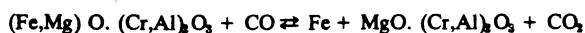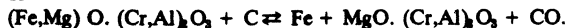
The reduction of chromium oxide to metal becomes feasible at a p_{o_2} of less than 10^{-7} atm.

$2(Fe,Mg) O. (Cr,Al)_2O_3 + {}^{40}/_7 CO \rightleftarrows \underline{Fe} + {}^3/_7 Cr_7C_3 + MgO.Al_2O_3 + {}^{34}/_7 CO_2$
or
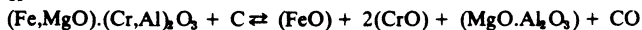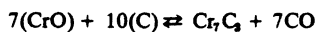$2(Fe,Mg) O. (Cr,Al)_2O_3 + {}^{34}/_7 C \rightleftarrows \underline{Fe} + {}^3/_7 Cr_7C_3 + MgO.Al_2O_3 + 4CO$.

Group III Dissolution of the chrome spinel in the slag phase at p_{o_2} values of less than 10^{-8} atm.

$(Fe,Mg) O. (Cr,Al)_2O_3 + CO \rightleftarrows (FeO) + 2(CrO) + (MgO.Al_2O_3) + CO_2$
or
$(Fe,MgO).(Cr,Al)_2O_3 + C \rightleftarrows (FeO) + 2(CrO) + (MgO.Al_2O_3) + CO$

$2Cr^{3+} + O^{2-} \rightleftarrows 2Cr^{2+} + O$ (simplified ionic equation)

$(C) + O \rightleftarrows CO$ (removal of oxygen to lower p_{o_2}).
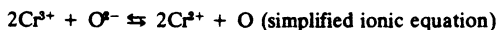
Group IV Reduction reactions

$(FeO) + (C) \rightleftarrows \underline{Fe} + CO$

$7(CrO) + 10(C) \rightleftarrows \underline{Cr_7C_3} + 7CO$

$(SiO_2) + 2(C) \rightleftarrows \underline{Si} + 2CO$.
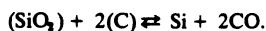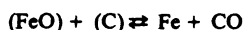
Parentheses indicate the slag phase
Underlining indicates the metal phase

furnace. Because of the chosen slow precession speed of about 50 r/min, they fell onto the surface of the bath without having much direct contact with the plasma arc. The anodic contact of the plasma arc with the surface of the bath, however, affords a good method of energy transfer to the endothermic reactions taking place. Precession of the arc distributes this energy across the surface of the melt. The fact that slags with low Cr_2O_3 contents were tapped from the furnace less than 5 minutes after the feed had been switched off, implies that the rates of reaction of the process are extremely rapid. Various reaction mechanisms were examined so that a reasonable explanation could be found for these results. It was found that these mechanisms formed two major groups, in one of which (solid-state reduction) the original spinel retains its form, whereas in the other the entire spinel dissolves. For convenience of reference these two types of reduction are referred to as Mechanism A and Mechanism B respectively.

Mechanism A

Several mechanisms have been proposed for the so-called solid-state reduction of chromium ore (12-15). However, in all instances, particle size, contact between the ore and the reducing agent, and (above all) temperature are probably the most important variables. Even though CO has been shown theoretically by Rankin (13) to reduce chromium ore, the rate of reaction is dependent on the close proximity of carbon for the reforming of CO_2 back to CO, i.e., for the maintenance of a sufficiently low partial pressure of oxygen (p_{O_2}). This process is very slow unless there is intimate mixing of the ore fines with a fine, reactive reducing agent. Solid carbon via the liquid metal phase has also been proposed by Barcza *et al* (12) as the reducing species and, as in the case where CO is considered, the particle size and particle contact are equally important (16). In view of this, it seems unlikely that sufficiently rapid rates of reaction could be achieved via solid-state reduction (either "in-flight" or on the surface of the bath) of these relatively coarse ore fines by coal chips. Re-

actions in groups I and II in Table VI descri[be] the reacting species more fully.

Mechanism B

A far more rapid process of reduction an[d] therefore more favourable mechanism is likely [to] occur when the oxides of iron and chromium dissolve in the slag and are reduced by solid carbon to produce metal and metal carbide - a[s] can be seen from the reactions in groups III a[nd] IV in Table VI. The dissolution of chromium [?] into the slag is therefore probably the key fa[c]tor in the establishment of this favourable pr[o]cess mechanism.

The solubility of the chrome spinel in t[he] slag, particularly that of the Cr_2O_3, is very limited under normal atmospheric conditions, [?] high values for p_{O_2} (17). Mineralogical inves[t]igation and laboratory-scale research work ha[s] established this fact (18). Figure 8 shows a typical example of undissolved chrome spinel [?] slag matrix. The values for chromium and iro[n] oxide in this slag were 26.3 and 12.7 per cen[t] respectively.
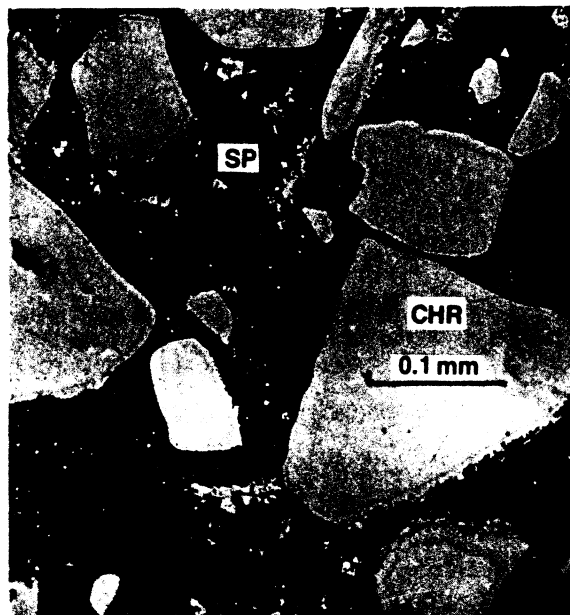

Figure 8. Chromite particles (CHR) virtually undissolved in the slag phase (the vitreous matrix material) and in a very early stage of alteration. Very little chromium-rich, recrystallized spinel (SP) is eviden[t]

At p_{O_2} values of 10^{-8} atm. and less, however, the solubility of Cr_2O_3 increases substantially according to Muan (17). Thus, chromium oxide can dissolve readily only in SiO_2 - Al_2O_3 - CaO - MgO slags of the compositions chosen during these tests at p_{O_2} values below 10^{-8} atm. Furthermore, a lowering of the liquidus temperature of the slag by some 200°C can occur, according to Muan (17), at a p_{O_2} of 10^{-12} atm. A CO-to-CO_2 ratio in excess of 10,000:1 is required for a p_{O_2} of 10^{-8} atm. to be met, and the presence of solid carbon is necessary to maintain such a high ratio of CO-to-CO_2. At elevated temperatures, this is feasible according to the Bouduard reaction (Table VI).

Since, in general, the approach of gas - liquid systems to equilibrium is relatively slow, it is unlikely that the gas phase will control the oxygen activity in the slag system under consideration. Metal phases that are present, especially chromium and silicon, have a far greater controlling influence on the activity of oxygen in the slag (19). The relevant reactions are shown in group III in Table VI. The object of successful smelting of high-carbon ferrochromium in a transferred-arc plasma furnace can therefore be realized only with a p_{O_2} value even lower than that required for the reduction of iron oxide (10^{-5} atm.) or chromium oxide (10^{-7} atm.). In fact, the p_{O_2} for the reduction of SiO_2 by carbon is about 10^{-9} atm., which is the same order of magnitude as that required for the dissolution of Cr_2O_3 in the slag. It follows then that, as long as a reasonable degree of reduction of SiO_2 is taking place, the p_{O_2} or oxygen activity in the melt must be low enough to ensure the dissolution of Cr_2O_3 as CrO in the slag phase. There is therefore a strong relation between the Si in the metal and the Cr_2O_3 content of the slag, and this is borne out by the graph in Figure 9. The oxygen activity in the slag is probably kept low by the removal of oxygen by solid, or possibly even dissolved, carbon. Mineralogical investigation of similar slags by use of an electron microprobe showed that dissolved carbon was present (18). This finding
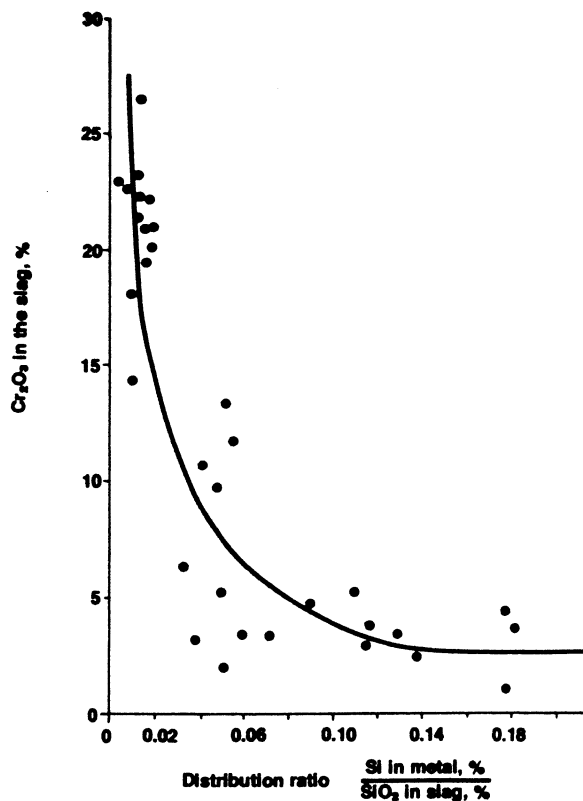

Figure 9. The relation between the silicon distribution ratio and the chromium oxide content of the slag based on results from the plasma trials

is consistent with those of other investigators (20).

The equilibrium relation for the two species of chromium oxide in the ionic equation in group III in Table VI is given by the following equilibrium constant (19),

$$K = \frac{a^2_{(Cr^{3+})} \cdot a_{(O^{2-})}}{a^2_{(Cr^{2+})} \cdot a_O},$$

where a is the activity of the species.

The lower the oxygen activity (a_O), the greater the Cr^{2+}-to-Cr^{3+} ratio, and therefore greater the solubility of chromium oxide in the slag. If there is insufficient carbon present remove the oxygen and to maintain the required low oxygen activity, the Cr_2O_3 in the spinel w not dissolve in the slag phase (Figure 8). Th dissolution and reduction of iron oxide is, ho
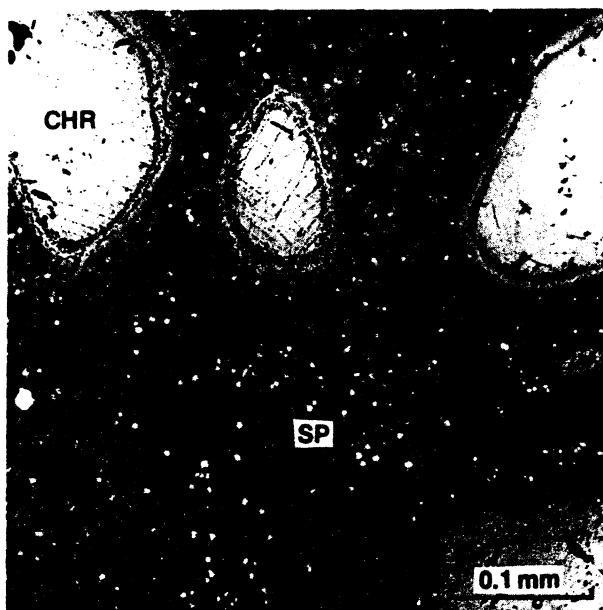
Figure 10. Chromite particles (CHR) mostly un-
dissolved but denuded of iron oxide
and therefore rich in chromium
oxide (53 per cent). Some re-
precipitated $MgO.(Al,Cr)_2O_3$ spinel
containing up to 30 per cent Cr_2O_3
is evident

Figure 11. No undissolved chrome spinel is
present, only recrystallized
$MgO.(Al,Cr)_2O_3$ spinel containing
moderate amounts of Cr_2O_3 (SP)
and pyroxene crystals (PX) in a
slag matrix. Widely distributed
metal blebs rich in chromium (MB
are associated with the re-
crystallized spinel.

Figure 12. Recrystallized $MgO.(Al,Cr)_2O_3$
spinel virtually free of chromiu
i.e., almost pure $MgO.Al_2O_3$ (SP)
Few metal blebs are evident, sho
ing that there was little CrO le
in the slag before it cooled, i.
the reaction was almost complete

ever, possible at higher p_{O_2}. Thus, residual
and altered, but virtually undissolved, spinels
rich in Cr_2O_3 (about 50 per cent) but with almost
no iron oxide (less than 5 per cent) remain in
the slag phase under moderately low p_{O_2} values,
as shown in Figure 10. The values for chromium
and iron oxide in this slag were 22.6 and 4.2 per
cent respectively showing that iron oxide has
been preferentially reduced. When the p_{O_2} is low
enough, the spinel will be fully dissolved in the
slag and the chromium oxide will react rapidly
with the carbon. Therefore, unless sufficient
carbon is present to maintain this low (a_0), the
Cr^{2+}-to-Cr^{3+} ratio will decrease and some Cr_2O_3
will exsolve from the liquid phase to form a solid
spinel phase ($MgO.(Al,Cr)_2O_3$), even at tempera-
tures as high as 1600 to 1700°C. Any CrO present
in the slag will become unstable on cooling, and
therefore dissociate to form chromium metal and
Cr_2O_3, which recrystalizes as an $MgO.(Al,Cr)_2O_3$
spinel. Finely divided chromium-rich metallic
blebs are associated with all the spinel part-
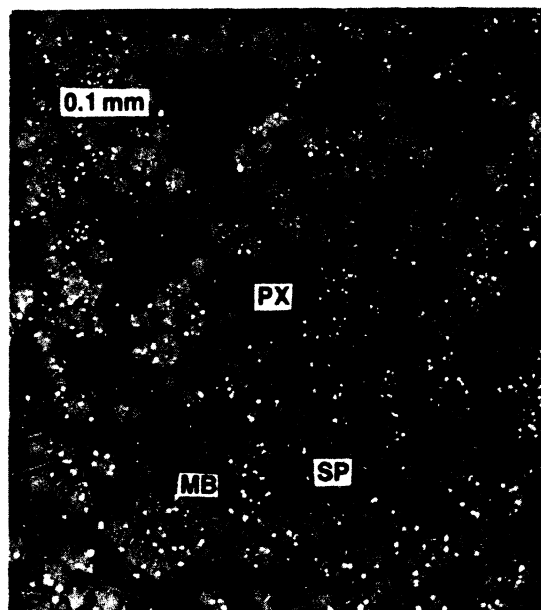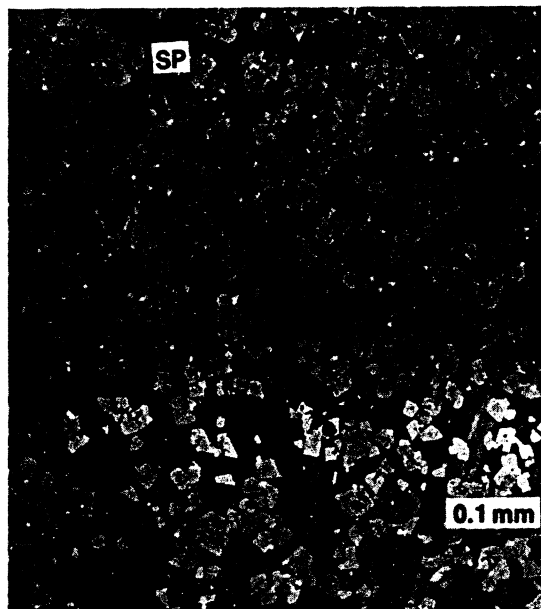icles distributed throughout the slag in Figure

11. The chromium and iron contents of this slag were 8.9 and 1.95 per cent respectively, showing that there was still a moderately large residual chromium oxide content. However, there was no undissolved spinel in this slag sample, indicating that the p_{O_2} value reached was low enough but had probably not been maintained throughout the test.

Figure 12 shows a slag in which the recrystallized spinel contains very little chromium oxide. Furthermore, there are virtually no chromium-rich metallic blebs, suggesting that nearly all the CrO had been reduced from the slag and that conditions close to equilibrium had been achieved. The analysis of this slag was 3.9 per cent Cr_2O_3 and 1.05 per cent FeO.

Summary

The chromium oxide (CrO) that can be dissolved (up to about 60 per cent by mass) in the slag will probably be reduced extremely rapidly by solid or dissolved carbon at temperatures exceeding the liquidus temperature of the slag (17). Hence, at these temperatures, the rate of reduction via Mechanism B is likely to exceed by far that via Mechanism A (21).

The process is therefore favoured by "in-bath" rather than by so-called "in-flight" reactions, since Mechanism B requires the solid or dissolved carbon to be in contact with a liquid slag containing dissolved iron and chromium oxides.

Mineralogical examination of slags taken from the plasma furnace during tests tend to support the above hypotheses, as do the many results obtained, which indicate that high recoveries of chromium and iron were achieved even when the furnace was tapped almost immediately after the feed had been stopped.

Future Developments

Existing submerged-arc furnaces represent a large capital investment, and it is unlikely that transferred-arc plasma furnaces will oust the conventional smelting methods in the near future,

despite the following cost benefits that could amount to a potential saving of some 20 to 30 cent.

1. The pre-treatment (i.e., pre-heating and possible pre-reduction) of chromium-ore fir would be potentially less costly than it i with the rotary-kiln process, since the pr heated ore fines from a fluidized-bed proce could be fed direct to the plasma furnace. This pre-treatment, which would take place outside the plasma furnace, would use hot off-gases from the furnace that contains, example, hydrocarbons from coal pyrolysis. As a result, less electrical energy, which expensive, would be required for the overal process.

2. The direct use of ore fines in the plasma furnace would avoid costly agglomeration methods such as pelletizing where the ore must be milled and the pellets fired. The production of briquettes is also fairly cos ly, and the briquettes partly break up in t submerged-arc furnace, causing relatively high losses to the slag of undissolved chro spinel.

3. The cost of coal fines, which would be used in the transferred-arc plasma furnace, is about one-fifth of the price of lumpy coke or char. Also, a valuable off-gas would be produced if they were used.

4. The controlled smelting in the liquid bath the transferred-arc system would favour rap reactions and high recoveries. This is in contrast to the results achieved so far in attempts to react chromium ores by the so-called "in-flight" approach, where recoveri of 46 per cent of the iron and only 7.3 per cent of the chromium have been realized (22 Recoveries for the TRD plasma system are some 30 per cent higher than those for the conventional submerged-arc furnace when chromite ores of the Transvaal type are smelted. The high throughputs made feasibl by the "in-bath" approach considerably decrease the size of furnace required. Furth

more, the absence of a solid burden still further reduces the size of furnace required. The limiting design criterion is likely to be the need for removal of the off-gas without entrainment of the solids. The ultimate design constraint in the minimization of furnace size is therefore the local gas velocity. Pre-reduction would effectively decrease the amount of gas evolved. A considerable capital saving is therefore likely should such plasma furnaces be constructed.

5. The cost of graphite or self-baking electrodes contributes substantially to the costs of consumable materials in the conventional process. If scale-up and the high reliability of plasma-arc guns were realized, there is little doubt that submerged-arc furnaces as known today would be phased out over the next few decades, and that new installations would incorporate features of the transferred-arc plasma system discussed in this paper.

Conclusions

1. The TRD transferred-arc plasma system produced on-grade high-carbon ferrochromium, with chromium recoveries of up to 98 per cent, from Transvaal chromium-ore fines. Such recoveries are not attainable in conventional submerged-arc furnaces.

2. The 1400 kVA scale of operation was sufficient to yield reliable mass and energy balances, but scale-up to some 20 to 30 MW would be necessary if plasma technology were to have any impact on the conventional submerged-arc furnace practice.

3. The potential benefits of this plasma system, which were demonstrated during the trials, are the following: the fact that fines can be treated direct, flexibility in regard to the choice of carbonaceous reducing agent, the low cost involved in maintenance of the water-cooled gun, and the improved controllability of the process, especially of its temperature.

4. The approach favouring "in-bath" instead of

"in-flight" reactions was found to be a s[uit]able method for the production of ferroch[rom]ium in a transferred-arc plasma system. [The] most likely process mechanism appears to [be] the rapid dissolution of chrome spinel at [high] p_{O_2} into the liquid slag phase, followed [by] the reduction, by carbon, of the dissolve[d] oxides of chromium and iron.

5. A large-scale transferred-arc plasma furn[ace] would probably be much smaller than an eq[ui]valent submerged-arc furnace because of t[he] rapid "in-bath" reactions and the avoidan[ce] of a burden. The limiting size factor wo[uld] probably be related to the off-gas veloci[ty] at which the entrainment of solids were a[t a] minimum. Problems in regard to the roof [re]fractory and the reliability of the plasm[a] gun could probably be solved.

6. The developments reported in this paper [have] paved the way for the erection - at TRD a[nd] at Mintek - of larger pilot plants rated [at] about 3.0 MVA. These facilities will be [used] to continue development work in new and existing plasma applications. MS&A have, however, decided to install a 10 MVA sem[i-] industrial scale unit based on the resul[ts] reported here.

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