THE PRODUCTION OF FERROCHROMIUM
IN A TRANSFERRED-ARC PLASMA FURNACE

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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 megavoltamperere 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
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 Tetrackics 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 series of trials on the plasma-arc facility at TRD. The facility was selected by MS&A and Mintek as a suitable pilot plant on which to conduct pyrometallurgical trials and to investigate the potential benefits of plasma for the smelting of high carbon ferrochromium from Transvaal chromite fines and fine carbonaceous reducing agents, especially cheap coal with high contents of and volatile materials.

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

Experimental Method

The overall layout of the test facility at TRD is depicted in Figure 1, and although several preliminary tests were carried out on a 300 kVA plasma furnace, the following description is of the more significant testwork done on a 1.4 MVA furnace.
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 Winterveldt 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 a composition of 12 per cent Cr₂O₃, 6 per cent Fe₂O₃, 35 per cent SiO₂, 0.35 per cent CaO, 19.3 per cent MgO, and 27.4 per cent Al₂O₃, 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

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Chromium Ore</th>
<th>Fluxes:</th>
<th>Carbonaceous Reducing Agents:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr₂O₃</td>
<td>FeO</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Winterveld chromite</td>
<td>44.6</td>
<td>23.3</td>
<td>2.23</td>
</tr>
<tr>
<td>0.1 &lt; (\bar{d}) &lt; 2.0 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>-</td>
<td>0.20</td>
<td>99.5</td>
</tr>
<tr>
<td>0.1 &lt; (\bar{d}) &lt; 0.7 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lime</td>
<td>-</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>0.01 &lt; (\bar{d}) &lt; 0.08 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\bar{d}\) = mean particle size, \(\text{mm}\)

< = less than
Table II - Feed compositions

<table>
<thead>
<tr>
<th>Recipe designation</th>
<th>Composition, mass % of the ore</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Winterveld ore</td>
<td>Quartz</td>
</tr>
<tr>
<td>SI/2</td>
<td>100.0</td>
<td>18.0</td>
</tr>
<tr>
<td>SI/5</td>
<td>100.0</td>
<td>19.0</td>
</tr>
<tr>
<td>SI/7</td>
<td>100.0</td>
<td>19.0</td>
</tr>
<tr>
<td>SI/8</td>
<td>100.0</td>
<td>19.0</td>
</tr>
<tr>
<td>S2/1</td>
<td>100.0</td>
<td>25.0</td>
</tr>
<tr>
<td>S3/1</td>
<td>100.0</td>
<td>20.0</td>
</tr>
<tr>
<td>S3/2</td>
<td>100.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

* S = Smelting recipe (SI = 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 furnace had fins, was used to maintain electrical contact with the internal molten bath.

Plasma Gun. In all essentials, the plasma gun, which is schematically depicted in Figure 3, was as described in the patent literature (9) and was mounted as shown in that Figure. It was precessed by a hydraulic motor at approximately 50 r/min at an angle of 9° from the vertical. Electrical current was supplied by a water-cooled lead from the services manifold to the plasma-gun cathode at up to 1250 A (briefly 1450 A). Argon gas from a bulk liquid storage tank was supplied at 3 to 4 Nm³/h, and de-I (0.5 mS/m) cooling water at a pressure of 670 kPa was used to remove between 20 and 35 °C of heat from the gun at a flow rate of between 3.5 m³/h with a maximum permissible outlet temperature of 55°C. A series of gun lengths between 380 and 500 mm were used during the trials, which yielded arc lengths of from 50 to 350 mm within the furnace.

Power Supply. A simplified drawing of the power supply is given in Figure 4. The step-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 output, which provided a suitable supply for a twelve-pulse thyristor-based rectifier. The thyristors were controlled by a constant-current circuit that formed the primary control of the power input to the process, whereas the overall resistivity of the arc itself had the largest process dependent effect upon the maximum power input. A series of interlocks that were automatically activated by a programmable logic controller (PLC) whenever any detectable malfunction (e.g., in the supply of argon gas) occurred, formed the background control function for the power supply and the plasma gun. The logic controller also carried out the sequential operations required to start up the plasma gun.

Auxiliaries. A table feeder was used with three "ploughs" that displaced material from the
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 analyzer (CO, CO₂, and O₂) 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.

**Table III**

**Metallurgical results**

<table>
<thead>
<tr>
<th>Recipe no</th>
<th>Input feed, kg</th>
<th>Output kg</th>
<th>Analysis of output, %</th>
<th>Thermodynamic energy consumption, kWh/t</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Ore</td>
<td>Quartz</td>
<td>Lime</td>
<td>Coal</td>
</tr>
<tr>
<td>S1/2</td>
<td>80.0</td>
<td>55.9</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td>S1/5</td>
<td>90.1</td>
<td>58.5</td>
<td>11.1</td>
<td>-</td>
</tr>
<tr>
<td>S1/5</td>
<td>340.1</td>
<td>220.8</td>
<td>42.0</td>
<td>-</td>
</tr>
<tr>
<td>S1/5</td>
<td>120.0</td>
<td>77.9</td>
<td>14.8</td>
<td>-</td>
</tr>
<tr>
<td>S1/5</td>
<td>375.0</td>
<td>243.5</td>
<td>46.3</td>
<td>-</td>
</tr>
<tr>
<td>S1/5</td>
<td>355.0</td>
<td>230.5</td>
<td>43.8</td>
<td>-</td>
</tr>
<tr>
<td>S1/5</td>
<td>380.1</td>
<td>246.8</td>
<td>46.9</td>
<td>-</td>
</tr>
<tr>
<td>S1/5</td>
<td>350.1</td>
<td>227.3</td>
<td>43.2</td>
<td>-</td>
</tr>
<tr>
<td>S2/1</td>
<td>647.0</td>
<td>417.0</td>
<td>104.0</td>
<td>-</td>
</tr>
<tr>
<td>S2/1</td>
<td>666.0</td>
<td>416.0</td>
<td>104.0</td>
<td>-</td>
</tr>
<tr>
<td>S1/7</td>
<td>620.0</td>
<td>372.0</td>
<td>70.0</td>
<td>-</td>
</tr>
<tr>
<td>S1/8</td>
<td>180.0</td>
<td>109.0</td>
<td>22.0</td>
<td>5.0</td>
</tr>
<tr>
<td>S3/2</td>
<td>656.0</td>
<td>353.0</td>
<td>113.0</td>
<td>17.0</td>
</tr>
<tr>
<td>S3/2</td>
<td>577.0</td>
<td>350.0</td>
<td>70.0</td>
<td>17.0</td>
</tr>
</tbody>
</table>

* The minimum energy required per ton of metal calculated from standard thermodynamic data

A = Four recipes combined: S1/2, S2/1, S1/8, and S3/1

**Legend:**

- Based on 3280 kWh/t per ton of metal
- Feed/metal ratio = 3.1:1
- Heat losses = 100 kWh
- Operating range = Typical operating region

**Furnace Operation**

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

Results

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 genuine 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](image)

![Figure 7. Hearth and roof temperatures during a steady run](image)
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 energy consumption, since this latter value is discussed in the section on operational results. Typical mass and energy balances for two of the tests are presented in Tables IV and V. A computer programme was used to calculate these outputs.

Discussion

In terms of the operation of the plasma system and of the metallurgical behaviour of the process, the performance of the furnace can be evaluated by consideration of the representation of cross-section of results given in Tables III I, II and Figures 5 and 6. The performance of the transferred-arc plasma system and especially the principles applied in the use of this equipment must be related to the conventional method for the production of ferrochromium in the submerged-arc furnace if a realistic comparison is to be made.
TABLE V

SMELTING BALANCE

<table>
<thead>
<tr>
<th>KG</th>
<th>CR2O3</th>
<th>FEO</th>
<th>STO2</th>
<th>CAN</th>
<th>MGO</th>
<th>AL2O3</th>
<th>CR</th>
<th>FE</th>
<th>BT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHROMITE</td>
<td>350.00</td>
<td>44.60</td>
<td>23.50</td>
<td>2.23</td>
<td>.20</td>
<td>11.20</td>
<td>13.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QUARTZ</td>
<td>70.00</td>
<td>0.00</td>
<td>.20</td>
<td>99.45</td>
<td>0.00</td>
<td>0.00</td>
<td>.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LIME</td>
<td>17.00</td>
<td>0.00</td>
<td>.04</td>
<td>.50</td>
<td>95.00</td>
<td>0.20</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COAL</td>
<td>140.00</td>
<td>0.00</td>
<td>.30</td>
<td>8.50</td>
<td>0.00</td>
<td>0.00</td>
<td>5.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>156.10</td>
<td>82.12</td>
<td>89.40</td>
<td>16.85</td>
<td>34.23</td>
<td>55.55</td>
<td>5.00</td>
<td>0.00</td>
<td>12.24</td>
</tr>
<tr>
<td>TOTAL &amp; FINES</td>
<td>156.10</td>
<td>82.12</td>
<td>89.40</td>
<td>16.85</td>
<td>34.23</td>
<td>55.55</td>
<td>5.00</td>
<td>0.00</td>
<td>12.24</td>
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<tr>
<td>TO METAL</td>
<td>149.47</td>
<td>79.59</td>
<td>21.40</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>102.24</td>
<td>61.64</td>
<td>10.24</td>
</tr>
<tr>
<td>TO SLAG</td>
<td>5.90</td>
<td>1.66</td>
<td>64.52</td>
<td>16.47</td>
<td>37.12</td>
<td>54.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMOKE LOSS</td>
<td>.73</td>
<td>.47</td>
<td>2.96</td>
<td>.34</td>
<td>2.12</td>
<td>1.11</td>
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</tr>
<tr>
<td>ANALYSIS(SLAG)</td>
<td>3.20</td>
<td>.90</td>
<td>35.00</td>
<td>5.40</td>
<td>26.10</td>
<td>27.10</td>
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</tr>
<tr>
<td>ANALYSIS(METAL)</td>
<td>56.52</td>
<td>34.18</td>
<td>1.29</td>
<td>5.00</td>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

Excess Carbon = 18.56 %

Recoveries As %

<table>
<thead>
<tr>
<th>CHROM</th>
<th>IRON</th>
<th>SILICON</th>
</tr>
</thead>
<tbody>
<tr>
<td>FROM ORE</td>
<td>49.75</td>
<td>46.95</td>
</tr>
</tbody>
</table>

Slag Forming Ratios

<table>
<thead>
<tr>
<th>SLAG FORMING RATIOS</th>
<th>MGO/SIO2</th>
<th>MGO/CAN</th>
<th>MGO/AL2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLAG</td>
<td>.75</td>
<td>4.83</td>
<td>1.96</td>
</tr>
</tbody>
</table>

MGO/STO2 | 1.30 |

Total Wt. of Slag = 149.47 Kg

Viscosity = .162 N.S./M.** (1.619 POISE)

Slag Liquidus Temperature = 1650 deg C

Metal Liquidus Temperature = 1555 deg C

Slag Conductivity = 4.7304 SEI/CM

Heat Balance Table (Based on the production of one metric ton of charge chrome)

<table>
<thead>
<tr>
<th>HEAT PROVIDED FOR</th>
<th>KJOULES</th>
<th>TEMPERATURES K</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEATING OF RAW MATERIALS</td>
<td>5091322.00</td>
<td>FROM 298.00 TO 1950.00</td>
</tr>
<tr>
<td>REDUCTION REACTIONS</td>
<td>4922152.00</td>
<td></td>
</tr>
<tr>
<td>FUSION OF METAL</td>
<td>496311.13</td>
<td></td>
</tr>
<tr>
<td>FUSION OF SLAG</td>
<td>912439.00</td>
<td></td>
</tr>
<tr>
<td>HEAT INPUT</td>
<td>11422724.00</td>
<td>3172.09</td>
</tr>
<tr>
<td>OFF-GAS HEAT LITERATED</td>
<td>231644.00</td>
<td>64.33</td>
</tr>
<tr>
<td>THERMODYNAMIC REQUIREMENT</td>
<td>11191080.00</td>
<td>3107.76</td>
</tr>
</tbody>
</table>

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 off-gas removal) so that an empirical approach to specific situations appears to be the best basis for the achievement of good operation. The situations obtained from the trial programme were that an arc length of between 0.4 and 0.5 m was similar gun length would produce reliable operation with recipes S1/5 or S3/1 at a voltage of between 450 and 550 V. A typical gun heat loss defined as being the power loss to the cooling water as a percentage of the maximum power, was 5.5 per cent, which was largely due to heat losses through the relatively large surface area of the nozzle. Maintenance of the plasma gun was not difficult because of its small size and replacement (usually less than 30 minutes). The replacement time could be improved upon if more sophisticated handling equipment for the plasma 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 always possible for the furnace contents to be removed completely after each batch operation, as already discussed above.

The first row of data in Table III shows that low values were obtained for chromium oxide in a batch test on the smaller 300 kVA facility when 80 kg of feed produced 30 kg of metal and 24 kg of slag containing only 2.5 per cent Cr₂O₃ 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 1600 kVA TRD plasma furnace. The recovery of chromium decreased dramatically with increasing feed rate, and hence the chromium oxide content of the slag increased from 14.4 per cent at a feed rate of 200 kg/h to 23.3 per cent at a feed rate of 350 kg/h.

The reason for the poor chromium recovery and therefore the high slag-to-metal ratio was thought to be related to a loss of carbonaceous reducing agent - in this case the coal - by one or both of two possible mechanisms.

1. Fine coal was entrained in the off-gas, and was removed from the furnace to be combusted in the off-gas duct.

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

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

The furnace was sealed more tightly, and additional inert gas was used to purge the feed system. The furnace was operated under slight positive pressure conditions to minimize the ingress of air, and a gas analyser was used to monitor CO, CO₂, and O₂.

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
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 of the smelting conditions. The very high recovery of chromium of 95.75 per cent, the low slag-to-metal ratio of 1.02, and the low "thermodynamic" energy consumption of 3108 kW.h per ton of metal in Table V afford confirmation that, when conditions are correctly controlled, favourable chemistry 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, limestone 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 \( p_{\text{O}_2} \) in the gaseous phase

\[
\begin{align*}
C + \frac{1}{2}O_2 & \rightleftharpoons CO \\
C + O_2 & \rightleftharpoons CO_2 \\
C + CO_2 & \rightleftharpoons 2CO \quad \text{(Boudouard reaction)} \\
CO + \frac{1}{2}O_2 & \rightleftharpoons CO_2.
\end{align*}
\]

**Group II** Solid state reductions on the surface of the bath. Iron oxide reduction becomes feasible at a \( p_{\text{O}_2} \) of less than \( 10^{-8} \) atm.

\[
\begin{align*}
(\text{Fe, Mg})O \cdot (\text{Cr, Al})_3O_4 + CO & \rightleftharpoons Fe + MgO \cdot (\text{Cr, Al})_3O_4 + CO_2 \\
or \ (\text{Fe, Mg})O \cdot (\text{Cr, Al})_3O_4 + C & \rightleftharpoons Fe + MgO \cdot (\text{Cr, Al})_3O_4 + CO.
\end{align*}
\]

The reduction of chromium oxide to metal becomes feasible at a \( p_{\text{O}_2} \) of less than \( 10^{-7} \) atm.

\[
\begin{align*}
2(\text{Fe, Mg})O \cdot (\text{Cr, Al})_3O_4 + \frac{4}{3} CO & \rightleftharpoons Fe + \frac{3}{2} \text{Cr}_7\text{C}_3 + MgO \cdot Al_4O_6 + \frac{4}{3} CO_2 \\
or 2(\text{Fe, Mg})O \cdot (\text{Cr, Al})_3O_4 + \frac{4}{3} C & \rightleftharpoons Fe + \frac{3}{2} \text{Cr}_7\text{C}_3 + MgO \cdot Al_4O_6 + 4CO.
\end{align*}
\]

**Group III** Dissolution of the chrome spinel in the slag phase at \( p_{\text{O}_2} \) values of less than \( 10^{-4} \) atm.

\[
\begin{align*}
(\text{Fe, Mg})O \cdot (\text{Cr, Al})_3O_4 + CO & \rightleftharpoons (\text{FeO}) + 2(\text{CrO}) + (MgO \cdot Al_4O_6) + CO_2 \\
or (\text{Fe, Mg})O \cdot (\text{Cr, Al})_3O_4 + C & \rightleftharpoons (\text{FeO}) + 2(\text{CrO}) + (MgO \cdot Al_4O_6) + CO
\end{align*}
\]

\[2C^{2+} + O^{2-} \rightleftharpoons 2Cr^{3+} + O \quad \text{(simplified ionic equation)}\]

\[(C) + O \rightleftharpoons CO \quad \text{(removal of oxygen to lower} \ p_{\text{O}_2}.\)]

**Group IV** Reduction reactions

\[
\begin{align*}
(\text{FeO}) + (C) & \rightleftharpoons Fe + CO \\
7(\text{CrO}) + 10(C) & \rightleftharpoons \text{Cr}_7\text{C}_3 + 7CO \\
(\text{SiO}_2) + 2(C) & \rightleftharpoons Si + 2CO.
\end{align*}
\]

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 \( \text{Cr}_2\text{O}_3 \) 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 \( \text{CO}_2 \) back to CO, i.e., for the maintenance of a sufficiently low partial pressure of oxygen \( (p_{\text{O}_2}) \). 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 Barca 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 reduction 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. Reactions in groups I and II in Table VI describe the reacting species more fully.

**Mechanism B**

A far more rapid process of reduction and 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 - as can be seen from the reactions in groups III and IV in Table VI. The dissolution of chromium oxide into the slag is therefore probably the key factor in the establishment of this favourable process mechanism.

The solubility of the chrome spinel in the slag, particularly that of the \( \text{Cr}_2\text{O}_3 \), is very limited under normal atmospheric conditions, i.e. high values for \( p_{\text{O}_2} \) (17). Mineralogical investigation and laboratory-scale research work has established this fact (18). Figure 8 shows a typical example of undissolved chrome spinel in the slag matrix. The values for chromium and iron oxide in this slag were 26.3 and 12.7 per cent 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 evident.](image-url)
At $p_{O_2}$ values of $10^{-8}$ atm. and less, however, the solubility of $\text{Cr}_2\text{O}_3$ increases substantially according to Muan (17). Thus, chromium oxide can dissolve readily only in $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{CaO}$ - $\text{MgO}$ 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 C0-to-CO$_2$ ratio in excess of 10,000:1 is required for a $p_{O_2}$ of $10^{-5}$ atm. to be met, and the presence of solid carbon is necessary to maintain such a high ratio of C0-to-CO$_2$. At elevated temperatures, this is feasible according to the Boudouard 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 $\text{SiO}_2$ by carbon is about $10^{-9}$ atm., which is the same order of magnitude as that required for the dissolution of $\text{Cr}_2\text{O}_3$ in the slag. It follows then that, as long as a reasonable degree of reduction of $\text{SiO}_2$ is taking place, the $p_{O_2}$ or oxygen activity in the melt must be low enough to ensure the dissolution of $\text{Cr}_2\text{O}_3$ as Cr0 in the slag phase. There is therefore a strong relation between the Si in the metal and the $\text{Cr}_2\text{O}_3$ 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 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),

$$K = \frac{a^2(\text{Cr}^{3+}) \cdot a(\text{O}_2^-)}{a^2(\text{Cr}^{2+}) \cdot a_0},$$

where $a$ is the activity of the species.

The lower the oxygen activity ($a_0$), the greater the $\text{Cr}^{2+}$-to-$\text{Cr}^{3+}$ ratio, and therefore the greater the solubility of chromium oxide in the slag. If there is insufficient carbon present to remove the oxygen and to maintain the required low oxygen activity, the $\text{Cr}_2\text{O}_3$ in the spinel will not dissolve in the slag phase (Figure 8). The dissolution and reduction of iron oxide is, how
Figure 10. Chromite particles (CHR) mostly undissolved but denuded of iron oxide and therefore rich in chromium oxide (53 per cent). Some re-precipitated MgO.(Al,Cr)2O3 spinel containing up to 30 per cent Cr2O3 is evident.

ever, possible at higher pO2. Thus, residual and altered, but virtually undissolved, spinels rich in Cr2O3 (about 50 per cent) but with almost no iron oxide (less than 5 per cent) remain in the slag phase under moderately low pO2 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 pO2 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 (aO2), the Cr2+-to-Cr3+ ratio will decrease and some Cr2O3 will exsolve from the liquid phase to form a solid spinel phase (MgO. (Al,Cr)2O3), even at temperatures 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 Cr2O3, which recrystallizes as an MgO. (Al,Cr)2O3 spinel. Finely divided chromium-rich metallic blebs are associated with all the spinel particles distributed throughout the slag in Figure 11.

Figure 11. No undissolved chrome spinel is present, only recrystallized MgO.(Al,Cr)2O3 spinel containing moderate amounts of Cr2O3 (SP) and pyroxene crystals (PX) in a slag matrix. Widely distributed metal blebs rich in chromium (MB) are associated with the recrystallized spinel.

Figure 12. Recrystallized MgO. (Al,Cr)2O3 spinel virtually free of chromium, i.e., almost pure MgO.Al2O3 (SP). Few metal blebs are evident, showing that there was little CrO left in the slag before it cooled, i.e., the reaction was almost complete.
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$_2$O$_3$ 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 per cent.

1. The pre-treatment (i.e., pre-heating and possible pre-reduction) of chromium-ore fines would be potentially less costly than it is with the rotary-kiln process, since the pre-heated ore fines from a fluidized-bed process 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, for example, hydrocarbons from coal pyrolysis. As a result, less electrical energy, which is expensive, would be required for the overall 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 costly, and the briquettes partly break up in the submerged-arc furnace, causing relatively high losses to the slag of undissolved chromium 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 of the transferred-arc system would favour rapid reactions and high recoveries. This is in contrast to the results achieved so far in attempts to react chromite ores by the so-called "in-flight" approach, where recoveries 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 feasible by the "in-bath" approach considerably decrease the size of furnace required. Further
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 entainment 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 suitable method for the production of ferrochromium in a transferred-arc plasma system. Most likely process mechanism appears to be the rapid dissolution of chrome spinel at P_O2 into the liquid slag phase, followed by the reduction, by carbon, of the dissolved oxides of chromium and iron.

5. A large-scale transferred-arc plasma furnace would probably be much smaller than an equivalent submerged-arc furnace because of the rapid "in-bath" reactions and the avoidance of a burden. The limiting size factor would probably be related to the off-gas velocity at which the entrainment of solids were at a minimum. Problems in regard to the roof refractory and the reliability of the plasma gun could probably be solved.

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

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