A New Route to Stainless Steel by the Reduction of Chromite Ore Fines in an Extended Arc Flash Reactor

By C. A. PICKLES, S. S. WANG, A. McLEAN, C. B. ALCOCK and R. S. SEGSWORTH

Synopsis

Literature pertaining to the beneficiation of low-grade chrome ores and the pyrometallurgical treatment of ore fines is reviewed. A description is then presented of a laboratory study in which molten iron-chromium alloys have been produced by reduction of chrome ore fines in an extended arc flash reactor. Low-grade coals have been used as reductants and no pelleting or briquetting of the material is required. The reactions pass through a rotary preheater, fall through a column of hot reducing gas, then through a high temperature plasma zone before collecting in the hearth where separation occurs between the metal and slag phases. Experiments were performed in which particular samples were withdrawn from various locations within the column and also after passing through the plasma zone in order to investigate liquefaction, spheroidization, phase separation and reduction sequences. The physico-chemical properties of the slags, slag-metal chemistry, metal quality and recoveries are reported and the implications of this process with respect to a new stainless steelmaking route are outlined.

1. Introduction

The principal use of chromium in the metallurgical industry is for the manufacture of alloy steels in which the chromium content varies from about 12 to 28%. High-carbon ferrochromium was initially produced by the reduction of chrome and chromiferous iron ore with coke or coal in a blast furnace. Some typical chrome ore analyses are listed in Table I. The main sources for these ores are Russia, Turkey, South Africa, and Rhodesia. A major improvement in the production of ferrochromium was the achievement of the high temperatures associated with the open-top submerged arc furnace in which the ore is generally used in lump form, and the energy required for melting and reduction is supplied primarily by resistance heating. In this type of furnace the electrical conductivity of the charge materials is an important consideration. Several review articles concerning the production of high-carbon ferrochromium are available in the literature.

The industrial consumption of low-carbon ferrochromium has decreased within the last eight years due to the development of the Argon Oxygen Decarburization Process (AOD). With this process it is possible to produce a low-carbon stainless steel from high-carbon ferrochromium and scrap by the selective oxidation of carbon. As the number of AOD vessels increases, the market for low-carbon ferrochromium will be reduced even further, and consequently, the market for the high-carbon alloy will increase.

While chrome ores are relatively widespread and abundant, many of the ore bodies are of poor quality and there is now an increasing scarcity of readily available, high-grade, lump ore. For these reasons, the beneficiation of low-grade chromites by tabling, flotation, high-tension electrostatic separation, and combinations of these processes, has been studied extensively. Many studies have also been made of both the fundamental and practical aspects of pyrometallurgical processes for increasing the chromium to iron ratio of the ore, frequently by selective reduction of the iron oxide fraction, followed by removal of the iron.

Since the success of the beneficiating processes depends to a large extent on the availability of a high

| Table I. Typical chrome ore analysis from different sources (wt%) |
|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Transvaal | Rhodesia | Turkey | Russian (high-grade) | Indian | Russian Ore | Russian Saranovskaya | American Midwest | Canadian |
| Chrome oxide (Cr₂O₃) | 45.0 | 54.0 | 48.0 | 55.0 | 49.5 | 55.0 | 42.4 | 38.6 | 45.3 |
| Ferrous oxide (FeO) | 26.0 | 15.0 | 14.0 | 12.5 | 14.5 | 12.5 | 14.9 | 21.6 | 23.2 |
| Lime (CaO) | 0.3 | 0.2 | 0.6 | 2.0 | 0.2 | — | — | 0.3 | 0.5 |
| Magnesia (MgO) | 11.0 | 13.0 | 17.5 | 16.5 | 15.5 | 16.6 | 17.4 | 15.3 | 1~10 |
| Alumina (Al₂O₃) | 15.0 | 11.8 | 13.0 | 8.0 | 11.0 | 8.8 | 12.2 | 15.7 | 10~20 |
| Silica (SiO₂) | 3.5 | 6.0 | 5.5 | 4.5 | 6.5 | 3.9 | 7.2 | 6.7 | 1~10 |
| Others, including H₂O | 0.3 | 0.2 | 1.3 | 1.5 | 2.8 | 3.2 | 5.9 | 1.6 | — |
| Cr/Fe ratio | 1.5 | 3.0 | 3.0 | 3.8 | 3.0 | 3.9 | 2.5 | 1.6 | 1.7 |

* including a very small amount of CaO
** 0.005%P, 0.022%S
*** 0.011%P, 0.021%S

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surface area to volume ratio of the particles, a high-grade, but fine-grained concentrate is produced. In addition, it is becoming necessary to use certain high-grade ores which are only available in a particulate form. In both cases, the materials must be agglomerated before treatment in a submerged arc furnace since the percentage of fines which can be included with the charge materials is usually less than 20%, -20 mesh. The deleterious effects of fines are more pronounced in large furnaces, and since furnace sizes have increased rapidly during the past twenty years, the influence of fines on furnace operation has become more critical. Agglomeration processes such as briquetting and pelletizing modifications in the design of electric smelting furnaces and a fluidized-bed electric arc furnace and rotating furnaces have all been suggested as possible solutions for the problems which are encountered during the processing of fines. A two-stage ferroalloy beneficiation process utilizing an arc heater has been proposed by Westinghouse for the treatment of low-grade chrome ore fines, while several other plasma-arc processes have been suggested for the reduction of metal oxide fines. Despite these efforts, even the most advanced types of electric smelting furnaces do not yet offer a complete solution to the problems associated with the use of unprepared raw materials.

In the present investigation, high-carbon ferrochromium was produced from chrome ore fines designated in Table 1 as Russian, Russian Saranovskaya, American and Canadian. For the plasma furnace described in this paper, the charge consists of 100% fines and pelletizing or briquetting steps are avoided.

II. Physical Chemistry Aspects

The physico-chemical properties of the slag phase such as liquidus temperature, viscosity and electrical conductivity are all important parameters in determining the efficiency of the conventional operation and consequently have been studied in some detail. Since the lime content is often insignificant, the slag can be considered in terms of the simple ternary system (SiO$_2$-Al$_2$O$_3$-MgO), the phase diagram for which is shown in Fig. 1. Typical slags from the production of high carbon ferrochrome contain these oxides in the ratio 1:1:1. Usually, chrome ores contain equal quantities of alumina and magnesia and the same ratio would be expected in the slag. However, in some cases the silica content can range from 20 to 45% and magnesia to alumina ratio from 0.67 to 1.5. When required, silica and alumina are added as fluxing agents. The slag compositions which melt in the range 1 600° to 1 700°C correspond to a silica content of 33 to 40%. The 1 600°C isotherm is parallel to the MgO-Al$_2$O$_3$ join and the 1 700°C isotherm inclines slightly toward the join. Thus, large changes in the MgO to Al$_2$O$_3$ ratio have only a minor effect on the melting point of the slag.

When the required composition of the slag used in the present investigation was 44%SiO$_2$, 24%Al$_2$O$_3$, and 23%MgO, then pure silica and alumina were added with the charge materials. From Fig. 1, it is clear that the liquidus temperature of this slag is about 1 600°C. Based on the results of Liutukov and Tsylinev, the viscosity of this slag was estimated to be about 6 poise at 1 600°C and 4 poise at 1 700°C, Fig. 2. When the required slag composition was 35%SiO$_2$, 29%Al$_2$O$_3$, 19%MgO, and 7%CaO, Alberta Hydro Flyash was added with the charge. Ossin et al. have measured liquidus temperatures, viscosities, and electrical conductivities of slags in this quaternary system. They also report the effects of chromium and iron oxide on these properties. In the case of the present work, these data indicate that the aim slag will have a liquidus temperature of about 1 600°C and a viscosity of approximately 3 poise.

For the reduction of chrome ores, the four most common reducing agents are solid carbon, and the gases: carbon monoxide, hydrogen and methane.
Thermodynamic considerations indicate that while iron oxide can be reduced by all of these reductants only carbon, hydrogen and methane are satisfactory agents for chromic oxide at conventional temperatures. Also, the reduction of chromium oxide is more readily achieved when metallic iron is present. Worrell has discussed in detail by Downing.55) Also, the reductant for chromic oxide at conventional temperatures. Only carbon, hydrogen and methane are satisfactory agents for chromium oxide can be reduced by all of these reductants.

Also, the reduction of chromium oxide is more readily achieved when metallic iron is present. Worrell has reported the Pourbaix-type diagram shown in Fig. 3, and the application of the data in this diagram to the thermodynamics of ferroalloy production has been discussed in detail by Downing.55) It can be seen, that if carbon is used as a reductant, the end product is usually chromium carbide rather than metallic chromium since the carbides have greater stability below 1800°C. Also, at constant total pressure the carbides with the lower carbon content become more stable as the temperature increases.

Geld and Esin have analyzed the equilibrium conditions during the reduction of iron chromite by carbon56) and also the kinetics of reduction of iron chromite and chromium oxide.57) These aspects have been investigated more recently by Lisniak et al.58-60) Boronenkov reports that the reduction of metals from molten slags by solid carbon may be explained in terms of the electrochemical nature of the reaction.61-63) The kinetics of reaction between particles of CrO3 and FeO has been examined by Maru.64) Barcza has studied the mechanism and kinetics of reduction of Transvaal chromite ores with carbon65) and the reduction of ferrous chromite by hydrogen has been investigated by the U.S. Bureau of Mines.66) Quayum and Reeve used methane-hydrogen mixtures to produce ferrochromium sponge from low-grade chromite ore.67) Read et al. have demonstrated that chromium sesquioxide can be reduced to either the metal or carbide by mixtures of hydrogen and methane,68) while Strater and Mantell have investigated the kinetics of hydrogen reduction of chromic oxide to metallic chromium.69)

III. The Extended Arc Flash Reactor*

A fundamental problem associated with conventional submerged arc smelting is the heavy losses which are incurred due to the low electrical resistance of the bath, as compared to the resistance of the shorted electrical circuit and the electrodes. Also, when the resistance of the charge is low, there is considerable branching of the current between the electrodes and this effectively limits the furnace voltage.39) Downing has shown that this charge resistance depends to a large extent on the slag composition and on the size and properties of the reducing agent.70) Another disadvantage of the furnace is the sharp temperature gradient which is generated between the highest temperature zone directly below the electrode tips and the lower temperature regions in the surrounding burden. Except for the melting of certain ferroalloys which have extremely high melting points, the temperatures generally required for melting are below 2500°C and the high local temperature of the electric arc is not required. Therefore, it would be advantageous if a more even temperature distribution could be achieved.31) These defects in the design of a submerged arc furnace can be overcome by the use of the Extended Arc Flash Reactor (EAFR), the general outline of which is shown in Fig. 4. The diameter of the hearth is about 200 mm while that of the graphite electrodes is 22 mm. The hearth zone is lined with a relatively high grade magnesia ramming mix, although carbon and graphite have also been used successfully. The arc is indirect and the metal and slag are heated by radiation from a soft diffuse plasma which is generated by the introduction of a small amount of gas through axial holes drilled in the graphite electrodes. The temperature distribution within this zone is relatively uniform, while the thermal conditions within the hearth zone can be controlled by adjustment of the flowrate and composition of the gas injected.

* U.S. Patent No. 4 006 284. Other patents pending.
through the electrodes. Under these circumstances, the electrical conductivity of the slag is no longer an important consideration. With plasma-flame heating, fluid slags are more readily obtained, slag–metal–reductant reactions are enhanced, and ferroalloys can be produced with low impurity concentrations. For these reasons, the EAFR system permits the use of a wider range of reductants than would be possible with conventional submerged arc smelting. In a typical test, the power input is 20 to 25 kW, three phase, with about 60 to 80 V, 60 Hz line to line, and a current of 150 to 200 A. The effective arc length (tip to tip) is in the range 80 to 150 mm.

A paper on the influence of Electrode-Gas-Injection on arc furnace steelmaking was presented at the 1976 ISS–AIME Electric Furnace Conference, while the treatment of steelplant waste oxides in the Extended Arc Flash Reactor was described at the 1977 IMM Symposium on Advances in Extractive Metallurgy. The application of the EAFR for the production of ferrochromium alloys from chrome ore fines is the subject of the present paper.

IV. Test Conditions

The chrome ore fines were mixed with the appropriate amount of carbonaceous reductant and flux additives, dried and heated to approximately 800°C by feeding through the preheater at a rate of about 10 kg/hr. This corresponds to a residence time of approximately 3 min and accelerates the reduction reactions in the other furnace zones. From the preheater, the charge falls under gravity through the reactor column where iron oxide is reduced by the counter-current flow of reducing gases which are formed within the hearth zone. The temperature in the lower portion of the reactor column is approximately 1600°C. On passing through the plasma zone particle temperatures exceed 2000°C, melting occurs and reaction rates are extremely fast. The metal and slag phases collect in the hearth where chromium oxide and any remaining iron oxide are reduced, after which both slag and metal phases are tapped through a single hole into a cast iron mold. After solidification the metal and slag are readily separated. Particle size analyses of the ores, reductants and flux additives are given in Table 2. Tables 3 and 4 provide the chemical composition of the reductants and flyash, respectively.

Before preparing the materials for smelting, a charge balance was performed using the method suggested by Robiette. The results of this calculation for Heat No. 3 are summarized in Table 5. This material balance also provides an estimate of the composition for both the slag and the ferroalloy. Test conditions for several heats with different ores are shown in

![Fig. 4. Extended Arc Flash Reactor (EAFR)](image)

<table>
<thead>
<tr>
<th>Mesh on</th>
<th>Russian</th>
<th>Russian Saranovskaya</th>
<th>American</th>
<th>Canadian</th>
<th>Alberta Hydro flyash</th>
<th>Coke</th>
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<td>8.2</td>
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<td>0.5</td>
<td>0.1</td>
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Table 2. Particle size analysis (wt%)
Table 6. Prior to Tests 1 and 2, the furnace was preheated for 1 hr whereas in the case of Test 3, the heat was made immediately after Test 2. Similarly, Test 6 followed immediately after Test 5. At the conclusion of a heat, metal and slag samples were taken for analysis from the solidified ingot, Table 7 and 8 respectively, and dust samples were removed from the preheater. Samples were cold mounted, polished and examined under the optical microscope.

Experiments were also conducted in which Canadian chromite ore was fed into the reactor through the preheater but without a carbon addition. Reducing gases were generated by adding anthracite periodically to the hearth zone. An alumina tube containing a 12 mm×6 mm cavity was placed within

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<th>Weight (g)</th>
<th>Cr (%)</th>
<th>Cr (g)</th>
<th>Fe (%)</th>
<th>Fe (g)</th>
<th>SiO₂ (g)</th>
<th>SiO₂ (g)</th>
<th>CaO (g)</th>
<th>CaO (g)</th>
<th>MgO (g)</th>
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<th>Al₂O₃ (g)</th>
<th>Al₂O₃ (g)</th>
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Calculated alloy analysis for specification: Cr+Fe=88%

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Total 694.3 100.0

Table 6. Typical test data

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<th>Ar flowrate (cfs)</th>
<th>Ore flowrate* (g)</th>
<th>alumina (g)</th>
<th>Silica (g)</th>
<th>Flyash (g)</th>
<th>Reductant** (g)</th>
<th>Feeding time (min)</th>
<th>Holding time (min)</th>
<th>Dust (g)</th>
<th>Slug (g)</th>
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* The ores used in these tests were as follows: Heats 1 to 3—500 g Russian and 1000 g Russian Saranovskaya; Heat 4—1500 g Russian Saranovskaya; Heats 5 and 6—2000 g American; Heat 7—2000 g Canadian.
** The reductants used in these tests were as follows: Heats 1 to 4—anthracite; Heats 5 and 6—graphite; Heat 7—coke.
*** Recovery is based on iron and chromium.
the reactor column to obtain samples of the chromite ore which were then transported by an argon stream into a collection vessel. These samples were cold mounted, polished and examined by optical microscopy in order to study the progress of reduction at different locations within the reactor column. The behavior of single particles in the column and plasma zones was investigated by feeding ore directly into the top of the reactor and bypassing the preheater. Test were performed in argon, carbon monoxide and hydrogen atmospheres. Quenched samples, unpolished and polished, were then examined with optical and scanning electron microscopy.

V. Reduction of Chromite Ores in the Flash Reactor Column

Photograph 1 shows the reduction of a low-grade chromite ore by carbon monoxide in the flash reactor column. The preheater is shown entering the column at the top. The degree of reduction increases progressively towards the plasma zone and fusion and liquefaction is indicated in the lowest position. These observations together with other results obtained from the heating of lump chromite ore in a carbon monoxide plasma have indicated a possible reduction mechanism which is in accord with previous studies where carbon was used as a reductant.\(^{(4,5)}\) In the temperature range 900\(^\circ\) to 1 000\(^\circ\)C serpentinite gangue minerals decompose into a dispersed intermediate product which then transforms into a granular, crystalline aggregate of olivine, (Mg, Fe\(_{2}\)SiO\(_4\)), with the migration of Fe\(^{2+}\) ions from the chromite spinel into the silicate bond. This silicate melts at about 1 400\(^\circ\)C.

(3) In argon atmospheres clusters of iron oxide droplets form on the chromite particles. At high magnification it can be seen that these small clusters are aggregates of spheres of the order of 1 \(\mu\)m in diameter (Photo. 4). These spheres may have been formed by the replacement of the iron oxide in the chromite by magnesium oxide from the magnesite:\(^{(26)}\)

\[
\text{FeO} \cdot \text{Cr}_2\text{O}_3 + \text{MgO} \rightarrow \text{MgO} \cdot \text{Cr}_2\text{O}_3 + \text{FeO}
\]

The replaced iron oxide would then separate on the

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Cr (%)</th>
<th>Fe (%)</th>
<th>C (%)</th>
<th>Si (%)</th>
<th>S (%)</th>
<th>P (%)</th>
<th>N (ppm)*</th>
<th>O (ppm)*</th>
<th>Total (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>58.48</td>
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<td>7.60</td>
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<td>0.014</td>
<td>0.005</td>
<td>53</td>
<td>111</td>
<td>99.11</td>
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<tr>
<td>2</td>
<td>59.61</td>
<td>26.60</td>
<td>7.18</td>
<td>6.42</td>
<td>0.010</td>
<td>0.023</td>
<td>141</td>
<td>74</td>
<td>99.84</td>
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<td>3</td>
<td>64.39</td>
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<td>1.76</td>
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<td>0.041</td>
<td>60</td>
<td>154</td>
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<tr>
<td>4</td>
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<td>0.036</td>
<td>28</td>
<td>66</td>
<td>94.65</td>
</tr>
<tr>
<td>5</td>
<td>50.90</td>
<td>25.06</td>
<td>8.12</td>
<td>15.50</td>
<td>0.007</td>
<td>0.064</td>
<td>18</td>
<td>118</td>
<td>99.67</td>
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<tr>
<td>6</td>
<td>50.23</td>
<td>35.11</td>
<td>7.86</td>
<td>6.35</td>
<td>0.009</td>
<td>0.060</td>
<td>35</td>
<td>98</td>
<td>99.62</td>
</tr>
</tbody>
</table>

* Inert gas fusion analysis

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Cr(_2)O(_3) (%)</th>
<th>FeO (%)</th>
<th>Al(_2)O(_3) (%)</th>
<th>SiO(_2) (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>P(_2)O(_5) (%)</th>
<th>C (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.12</td>
<td>3.73</td>
<td>22.19</td>
<td>12.66</td>
<td>2.69</td>
<td>34.17</td>
<td>0.009</td>
<td>---</td>
<td>80.56*</td>
</tr>
<tr>
<td>2</td>
<td>4.86</td>
<td>2.45</td>
<td>27.80</td>
<td>20.24</td>
<td>9.10</td>
<td>33.98</td>
<td>0.019</td>
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<td>98.45</td>
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<tr>
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<td>1.73</td>
<td>2.45</td>
<td>18.91</td>
<td>24.40</td>
<td>10.90</td>
<td>41.45</td>
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<tr>
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<td>44.70</td>
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<td>---</td>
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<td>4.76</td>
<td>---</td>
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<td>---</td>
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<tr>
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<td>5.55</td>
<td>6.12</td>
<td>---</td>
<td>38.96</td>
<td>---</td>
<td>0.014</td>
<td>0.41</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* This relatively low value may be due to uncertainties in the analysis of this particular slag.
surface of the chromite grains. This process is accelerated with increasing temperature\textsuperscript{27} and is analogous to that associated with the bursting of chromite magnesite refractories.

(4) Reduction occurs when either carbon monoxide or hydrogen is injected into the flash reactor. Photograph 5 shows chromite ore particles after falling through a carbon monoxide plasma. Metallic iron is found within the low melting point magnesium-silicate phase. No metallic iron was observed within the chromite crystals. No reduction of chromium oxide will occur in the carbon monoxide atmosphere. Spherical particles, which had obviously melted, did not contain metallic iron. This indicates an inhibition of the reduction reaction by complete liquefaction. This phenomenon has also been observed in
Iron ore reduction studies at high temperatures.\(^7\tag{8}\) In some cases, spherical iron droplets were attached to chromite ore particles (Photo. 6). It is suggested that these iron droplets are formed by the replacement of FeO in the MgO (as discussed previously) and subsequent reduction of the FeO on the surface of these particles.

Photograph 7 shows chromite ore particles reduced in hydrogen. In this case, the spherical chromite ore particles are reduced internally, and qualitatively the degree of reduction is much greater than that observed in the carbon monoxide atmosphere. Reduction is observed in areas where no cracks or phase separation is evident. Also, reduction at the edges of chromite grains is indicated. These beneficial effects can be attributed to the high diffusivity of hydrogen. Photograph 8 shows a metal sphere which was obtained during the hydrogen tests. X-ray fluorescence analy-
sis shows that the sphere contains chromium, iron and silicon. This confirms that chromium oxide and silica can be reduced in a hydrogen atmosphere when iron is present to decrease the activity of the reaction products.

When hydrogen is injected through the electrodes the plasma becomes unstable and the arc length must be shortened. Also, the plasma becomes constricted (i.e., its volume is reduced) and this results in inefficient heating of the particles. Consequently, the number of spherical particles is decreased. However, these effects can be minimized by preheating the hydrogen before it enters the plasma. This could be efficiently accomplished by injecting the hydrogen into the metal phase in the hearth of the furnace. This not only preheats the gas but it also increases reaction rates in the hearth. Urquhart reports that the generation of carbon monoxide causes active bubbling in the
slag and the mechanism of dissolution of chromium oxide changes from a first order to a higher order reaction.\textsuperscript{75b} This effect of stirring has also been observed in studies on the rate of removal of FeO from slags.\textsuperscript{79-81}

\textbf{VII. Smelting of Chromite Ore Fines}

Metal and slag analyses for six typical heats are shown in Tables 7 and 8. In the case of Heat 3, the chromium and iron concentrations of 64\% and 24\%, respectively, are in good agreement with the predicted values of 63 and 25 shown in the charge balance (Table 5). The carbon content is higher by about 1\% and the silicon content lower by about 3\% due to a relatively low operating temperature. The actual quantity of alloy produced was about 6\% below that calculated in the charge balance, although in terms of actual weight, this loss amounted to only 42 g. In the case of the slag phase, the increase in weight over that anticipated, is due to partial dissolution of the magnesia lining and mechanical entrainment of runner refractory during tapping. In each heat the chromium oxide and iron oxide contents of the slag are low. Photograph 9 shows the negligible amount of metal droplets entrained in the slag. This would confirm that slag fluidity was high and the holding time sufficient to allow effective metal separation. Typical micrographs of the metal phase, both etched and unetched are shown in Photo. 10. The alloy is dense in appearance and free from inclusions.

\textbf{1. Silicon}

The silicon content of ferrochromium is determined by slag basicity, operating temperature (i.e., energy consumption) and metal composition. Table 7 shows that when an acid slag is used (for example Heat 5), the silicon content of the ferrochrome, as expected, is much greater than that found with a basic slag. It can also be seen that as the operating temperature increases, the silicon content increases for both the acid and basic slags. Figure 5 shows the silicon–carbon relationship in ferrochromium alloys. As the
silicon content increases the carbon level decreases. This is in accord with the following reaction between silicon and chromium-iron carbides:

\[(\text{Cr, Fe})_6\text{C}_3 + 7\text{Si} = 7(\text{Cr, Fe})_\text{Si} + 3\text{C}\]

Heat 5 in which the silicon content was about 15% demonstrates that ferrochromium silicide alloys can also be produced by the flash reactor process.

2. Sulfur

Since carbon increases the activity coefficient of sulfur, high carbon alloys will tend to be low in sulfur. However, this effect is somewhat offset by the fact that chromium lowers the activity coefficient of sulfur in the metal. Table 9 shows that sulfur recovery in the ferrochromium alloys is about 2%, with a slag containing less than 25% silica (Heats 1 to 4) and about 6% when the silica content is in the range 40 to 50% (Heats 5 and 6). It can be seen that as the silicon content of the alloy increases the sulfur content decreases for both the acid and basic slags. This is attributed to the formation of volatile SiS. Similarly, an increase in energy consumption results in a decreased sulfur content due to the increased stability of SiS and the increased desulfurization potential of the slag. Kadarmetov et al. report that in a submerged arc furnace some sulfur may volatilize in this fashion and be recycled by condensation on the descending charge. This effect does not occur in the EAFR during the holding period so that some sulfur is removed with the off-gases. This is confirmed by the high sulfur content found in the exit dust (Photo. 11).

![Photo. 11. X-ray scan of the dust removed from the preheater of the EAFR (x9/10)](image)

![Table 9. Sulfur recoveries](chart)

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>Chromite ore weight (g)</th>
<th>Reducant weight (g)</th>
<th>S in charge (g)</th>
<th>Metal weight (g)</th>
<th>S in metal (wt%)</th>
<th>S in recovery (wt%)</th>
<th>Recovery in metal (%)</th>
<th>Slag SiO(_2) content (wt%)</th>
<th>Metal Si content (wt%)</th>
<th>Specific energy consump. (kW-h/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>500</td>
<td>3.82</td>
<td>564</td>
<td>0.014</td>
<td>0.079</td>
<td>2.1</td>
<td>12.66</td>
<td>4.5</td>
<td>0.032</td>
</tr>
<tr>
<td>2</td>
<td>1500</td>
<td>400</td>
<td>3.12</td>
<td>547</td>
<td>0.010</td>
<td>0.055</td>
<td>1.8</td>
<td>20.24</td>
<td>7.0</td>
<td>0.022</td>
</tr>
<tr>
<td>3</td>
<td>1500</td>
<td>450</td>
<td>3.47</td>
<td>652</td>
<td>0.010</td>
<td>0.065</td>
<td>1.9</td>
<td>24.40</td>
<td>2.4</td>
<td>0.012</td>
</tr>
<tr>
<td>4</td>
<td>1500</td>
<td>450</td>
<td>3.15</td>
<td>556</td>
<td>0.004</td>
<td>0.022</td>
<td>0.7</td>
<td>7.40</td>
<td>6.4</td>
<td>0.032</td>
</tr>
<tr>
<td>5</td>
<td>2000</td>
<td>500</td>
<td>1.00</td>
<td>971</td>
<td>0.007</td>
<td>0.068</td>
<td>6.8</td>
<td>48.52</td>
<td>15.5</td>
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</tr>
<tr>
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<td>2000</td>
<td>750</td>
<td>1.28</td>
<td>927</td>
<td>0.009</td>
<td>0.083</td>
<td>6.5</td>
<td>38.96</td>
<td>6.4</td>
<td>0.009</td>
</tr>
</tbody>
</table>

*Charge represents the weight of chromite ore and flyash.

![Table 10. Phosphorus recoveries](chart)
3. Phosphorus

Table 10 gives the phosphorus distribution for five of the heats reported. As expected, the phosphorus content of the metal increases with the phosphorus content of the raw materials and with increasing silica in the slag phase.

Robiette reports that about 80% of the phosphorus in the raw materials is usually recovered in the ferroalloy.\(^{19}\) Table 10 shows that the phosphorus recoveries in the metal phase from the flash reactor are consistently below 80%, even in Heat 5 where the Y ratio is less than one. In Heat 2 with a slag of higher basicity the recovery is less than 60%. These low recoveries can be attributed to the high slag fluidity and vigorous slag–metal mixing which promote dephosphorization in the hearth region of the EAFR. In Heat 3 the phosphorus distribution ratio is further decreased by the high slag volume.

Generally, high operating temperatures in practice correspond to a high recovery of phosphorus in the metal phase. This behavior was not observed with the EAFR. In Heat 1 the phosphorus content of both the slag and metal phases are extremely low (0.004 and 0.005%, respectively). The combined phosphorus recovery in the slag and metal does not exceed 30%. This would suggest, particularly in view of the high temperatures in the hearth zone, that considerable amounts of phosphorus were volatilized at the slag/gas interface and removed in the exit gases.

4. Nitrogen

The nitrogen content of ferrochromium is to a large extent determined by the nitrogen content of the reducing agent, the arc atmosphere, the metal composition and the extent of the carbon monoxide boil. Table 7 indicates that the nitrogen level in the metal is decreased by about 50% when anthracite containing 0.89% nitrogen is replaced by graphite containing 0.001% nitrogen. By Electrode Gas Injection with argon or a reducing gas, it is possible to displace nitrogen from the arc zone, and this prevents nitrogen absorption within this potentially active region. On the other hand, by generating a plasma with nitrogen or gas mixtures containing nitrogen, it is possible to increase the nitrogen content of molten alloys beyond that which would be in equilibrium with the same gas mixture in a non-plasma condition. The implications of this aspect of Electrode Gas Injection have been discussed in more detail elsewhere.\(^{22}\)

Carbon and silicon both increase the activity coefficient of nitrogen and thus for a given activity, the nitrogen concentration in the melt will tend to decreases. Chromium on the other hand, decreases the nitrogen activity coefficient, and thus its activity. For this reason, nitrogen removal to very low levels from high chromium alloys is particularly difficult. If the ferroalloy is to be used for the production of extra-low nitrogen, high chromium stainless steel, it is essential that the nitrogen content of the ferrochromium be maintained at as low a level as possible. In this respect, the agitation provided by carbon monoxide generation within the hearth of the flash reactor is beneficial in removing any nitrogen which might be picked up from the reducing agent.

VIII. Direct Conversion to Stainless Steel

The molten ferrochromium alloys produced from both the high and low grade ores could be charged directly to a converter, AOD unit or vacuum vessel for decarburization, scrap and alloy additions. With this processing route (Fig. 6), the heat content of the molten ferrochromium would be used to full advantage. Also, in the conventional submerged arc furnace process the solidified metal must be crushed and sized to meet certain specifications. During the crushing stage, fines are generated which have little commercial value. This operation is eliminated if the molten alloy is refined directly.

It should be noted, that for stainless operations of this description, leaner ores which would not be considered profitable for the production of high-grade ferrochromium additives, can be advantageously employed to yield molten alloys with a chromium to iron ratio closer to that of the final steel. It has been demonstrated in the laboratory that by adding the correct proportions of oxides to the EAFR it is possible to make a high-carbon alloy containing chromium, nickel, manganese and molybdenum with low residual concentrations of sulfur, phosphorus and nitrogen. This product would only require decarburization to yield stainless steel.

In this way the EAFR in tandem with a refining vessel, could provide a direct route from ore fines, through molten iron–chromium–nickel to stainless steel without the requirement for remelting in a high-powered arc furnace. The energy requirement for the reduction step as observed in the laboratory tests was about 12 000 kWh/t. This is only greater by a factor of three than that generally observed in regular production. From an energy viewpoint, this is most encouraging, when one considers the small scale of the existing unit, the high heat losses and the non-continuous nature of the present experiments.

IX. Conclusions

An extensive laboratory program has determined

![Fig. 6. A comparison between the conventional and extended arc routes to stainless steel](image-url)
that the Extended Arc Flash Reactor offers a number of features which could be exploited to advantage in a commercial application. These include:

1. The feed material is relatively fine (100% 0.35 mesh). Pelletizing or briquetting of the charge is not required and advantage can therefore be taken of the high surface area/volume ratio of the particles to enhance reaction rates.

2. The process is not sensitive to the composition of the raw material. Both high-grade ores, as well as low-grade materials which would not normally be considered amenable to treatment by conventional routes, can be readily processed in the EAF.

3. The process is not sensitive to the resistivity or size of the reductant. Bituminous coal, anthracite, coke, coke breeze, and graphite have all been employed successfully.

4. With Electrode-Gas Injection the electrical efficiency and power factor are significantly greater than those associated with conventional submerged arc furnace practice.

5. Metallurgical control of the ferrochrome product follows well-established procedures.

6. The Extended Arc Facility is relatively simple and not capital-intensive. Aside from the previously outlined operating details, very little new technology is involved. Power supply, materials handling and tapping operations are all conventional.

7. It is possible that the EAF in tandem with an appropriate converter or ladle furnace could produce stainless steel directly. In this way, crushing of the solidified ferrochromium with the generation of fines would be avoided, thermal energy would be conserved, and the remelting operation which is generally performed in an expensive arc furnace facility would be eliminated.

8. Since the nitrogen, sulfur and phosphorus levels of the molten ferrochromium are lower than those generally obtained with conventional practice, subsequent refining of the molten alloy offers the opportunity of manufacturing extremely low residual, ferritic stainless grades, which could not be produced by conventional steelmaking routes.

9. It is considered that an integrated ore to stainless steel operation of this type should be economically viable even on a relatively modest scale.

Acknowledgements

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