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The Application of a Laboratory Induction Furnace to the Selective Smelting of a Montana Chromite Concentrate

James H. McMahon

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THE APPLICATION OF A LABORATORY INDUCTION FURNACE TO THE
SELECTIVE SMELTING OF A MONTANA CHROMITE CONCENTRATE

A Thesis
Submitted to
the Department of Metallurgy
Montana School of Mines

In Partial Fulfillment
of the Requirements for the Degree
Bachelor of Science in Metallurgical Engineering

by
James H. McMahon
May 1, 1942
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<tr>
<td>Smelt six</td>
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CHAPTER I

THE PROBLEM AND ORGANIZATION OF THESIS

The existence of rather extensive (20)* low-grade deposits of chromite in south central Montana has been known for a long time. Due to the increased demand for chromium in the present war emergency and the uncertainty of a continued supply of foreign ores, these deposits have become extremely important. Since their recent development these ores are being mined and milled.

The Problem

The purpose of this experimental work was to determine with the utilization of a laboratory sized induction furnace a method whereby a high-iron Montana chromite concentrate could be successfully smelted to yield a product suitable for the subsequent production of standard ferrochrome.

Importance of the Work

To justify this work by revealing its importance the following section of this chapter will deal with the present ferrochrome situation. Technical, economic,
and political aspects will be considered.

In the manufacture of ferrochrome custom has established certain minimum specifications on the chromic oxide content and the ratio of chromium to iron in the raw material used. The former requirement is necessary to keep at a minimum the quantity of material undergoing treatment in producing a given amount of ferrochrome. The latter requirement is necessary, say the steel manufactures, to produce a ferrochrome sufficiently high in chromium to not excessively chill the molten steel bath when the alloy is added. In addition to this, iron increases the fusibility of chromite making it less desirable as a refractory.(22)

Until recently specifications demanded an ore which would yield a ferrochrome containing 68 to 69 per cent chromium, 4 to 6 per cent carbon, and 1 to 2 per cent silicon. Only foreign ore would produce a ferrochrome meeting these specifications. Imports have been mainly from Southern Rhodesia, Turkey, India, Cuba, New Caledonia, Greece, and the Philippine Islands.

Although the United States is by far the world's greatest consumer of chromite(15), it has produced less than one per cent of its needs. Shipments from domestic mines in 1940 were but 2662 long tons of ore 35 per cent Cr₂O₃ or better. Of 657,689 long tons of chromite shipped to
the United States in 1940, 156,556 long tons were from the Philippine Islands. Of the total export from the Philippine Islands in that year 194,393 long tons, 18.7 per cent, went to Japan.

Imports for the first nine months of 1941 (4) were 660,436 long tons compared with the above 657,689 long tons for the entire year 1940. The increased rate of foreign ore entry in 1941 was due mainly to shipments from Cuba, Africa, and the Philippine Islands. Domestic production of chromite in 1941 totaled over 12,000 long tons against the above 2662 long tons in 1940 and 273 long tons in 1936.

Any change of specifications as to the quality of domestic chromite ores by the governmental agency accordingly has its effect on this work. In a letter (16) issued by the Metals Reserve Company of the Reconstruction Finance Corporation on November 14, 1941 specifications were established regarding contracts for the purchase of domestic ore. The company considered two grades for contracts: 45 per cent Cr₂O₃ with a chromium-iron ratio of 2.5:1 and 40 per cent Cr₂O₃ with no minimum chromium-iron ratio. For the high-grade maximums on silica, phosphorus, and sulphur of 11 per cent, 0.2 per cent, and 0.5 per cent were established. For the low-grade ore a maximum of 8.0 per cent was established on the
silica with no maximum on the phosphorus and sulphur.

On December 19, 1941 a new schedule(4) established two types of the 40 per cent Cr₂O₃ grade. Present specifications are as follows:(3)

**TABLE I**

**DOMESTIC CHROMITE SPECIFICATIONS**

<table>
<thead>
<tr>
<th></th>
<th>High-grade</th>
<th>&quot;A&quot;</th>
<th>Low-grade</th>
<th>&quot;B&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃ -- min.</td>
<td>45.0</td>
<td>40.0</td>
<td>40.0</td>
<td></td>
</tr>
<tr>
<td>Cr:Fe -- min.</td>
<td>2.5:1</td>
<td>2:1</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>Silica -- max.</td>
<td>11.0</td>
<td>8.0</td>
<td>no max.</td>
<td></td>
</tr>
<tr>
<td>Phosphorus -- max.</td>
<td>0.2</td>
<td>no max.</td>
<td>no max.</td>
<td></td>
</tr>
<tr>
<td>Sulphur -- max.</td>
<td>0.5</td>
<td>no max.</td>
<td>no max.</td>
<td></td>
</tr>
</tbody>
</table>

Some higher grade foreign ores contain up to 55 per cent Cr₂O₃.

Until recently the ferrochrome producers maintained the ore standard of a 3:1 chromium-iron ratio. The silica content had been limited to 5 per cent.(15)

Also in December 1941 the American ferrochrome manufactures voluntarily agreed(4,17) to changes in specifications, to permit the use of lower grade chrome ores, and to conserve higher grades. Previous specifications of 68 to 69 per cent Cr, 4 to 6 per cent C, and 1 to 2 per cent Si were changed to 60 to 63 per cent Cr, 6 to 8 per cent C, and 4 to 6 per cent Si.
The new specifications, representing a return to those of twenty years ago, will allow the use of lower grade ores.

The above figures are for high-carbon ferrochrome. The production of low-carbon ferrochrome requires special treatment and is not directly related to this work. Ferrochrome containing down to 0.06 per cent carbon is a standard product today.\(^9\)

A complete reduction of an ore or concentrate having a chromium-iron ratio of 2.5:1 would result in a ferrochrome of 71.5 per cent Cr; however, complete recovery of chromium is never attained.

The Stillwater deposits in south central Montana have long been known to contain a large tonnage of ore of such low grade and low chromium-iron ratio as to prevent exploitation. However, due to the present emergency, they are now being developed to such an extent that they will make a large contribution to the elimination of the shortage of chromium in this country.

The ore from these deposits runs only 29 per cent \(\text{Cr}_2\text{O}_3\), but by gravity concentration at the mine a 45 per cent \(\text{Cr}_2\text{O}_3\) concentrate is anticipated having a chromium-iron ratio of 2:1.

The experiments carried out in this work were on a chromite concentrate from these Montana deposits.
The concentrate had a Cr$_2$O$_3$ content of 43.15 per cent and a chromium-iron ratio of only 1.47:1. Accordingly, it falls under the above classification Low-grade "B" in Table I.

If this concentrate were treated in the usual manner to produce ferrochrome and a complete recovery of chromium were attained, the percentage of chromium in the resulting alloy would then be only 59.5 falling short of the revised specifications of the American ferrochromium manufactures. However, such concentrates are undergoing enrichment by the addition of high grade material. This is an emergency step which probably will not continue, following the cycle of twenty years ago.

The purpose of these experiments, therefore, was to determine by laboratory means, which include the use of an induction furnace, a method whereby this Montana chromite concentrate could be successfully smelted to yield a product suitable for the subsequent production of a standard ferrochrome. A successful smelt would be one possessing that economic and metallurgical balance which would place the product on a competitive basis with the high grade foreign ores in peace time. Montana would thus be assured of a permanent chromium industry.
Organization of Thesis

In Chapter I the problem was stated, and justification for the work was presented.

Chapter II deals with a review of literature on other attempts to manufacture a product from low-grade chromite ores economically suitable for use in the steel industry.

Chapter III includes a description of physical, chemical, and mineralogical characteristics of the concentrate and methods employed in their determination. The induction furnace is described and its operation is explained. The method of procedure used in applying this furnace to the problem is outlined.

Chapter IV presents the execution and results of the experiments.

In Chapter V the results are summarized and conclusions drawn therefrom. Recommendations for further work are made.
CHAPTER II

REVIEW OF THE LITERATURE

This chapter deals briefly with published attempts by various investigators to treat the low-grade domestic chromite ores.

United States Bureau of Mines

(10) Some earlier experiments have been conducted on high-iron Montana chromite concentrates by the United States Bureau of Mines using an induction furnace with a graphite crucible. The disadvantage of allowing the reduced metal to be in contact with a large surface of white hot graphite was encountered; alloys were always saturated with carbon. The reduction of a concentrate containing 44.66 per cent $\text{Cr}_2\text{O}_3$ was attempted with coal using sand and fluorspar as fluxes. The conclusion was drawn that such domestic ores can be reduced with anthracite to produce a ferrochrome containing 8 to 10 per cent carbon and 80 per cent of the chromium without re-treating the slag. However, the low chromium-iron ratio was changed only to a slight extent in the reduction.

More recent investigations by the United States Bureau of Mines (25) entailed a selective reduction
of iron from a Montana chromite concentrate using coke in a pilot electric furnace. The resulting slag contained 40.2 per cent Cr₂O₃ and had a chromium-iron ratio of 2.7:1. This slag, when poured to a second pilot furnace at a temperature of 1650° to 1700°C, was reduced by petroleum coke to a standard ferrochrome. The first metal contained 40 per cent of the iron and only 8 to 10 per cent of the total chromium. This 20 per cent chromium metal was stated to be of value in the production of heat-resistant castings.

Chromium Mining and Smelting Corporation

A major investigator of the low-grade chromite problem, Marvin J. Udy of the Chromium Mining and Smelting Corporation, Sault Ste. Marie, Ontario, presented a paper (23) to the Canadian Institute of Mining and Metallurgy in 1938 concerning the Corporation's investigations on this problem.

The procedure in one method involved a selective reduction of the iron present in the ore by replacing FeO with a base such as CaO and by obtaining the greater part of the iron as the metal. (More recently (2,24), Udy states that when chromite ores are treated in this manner, it appears that MgO in the silicate is replaced by the lime, and in turn the MgO replaces FeO in the
Coke was added in the charge to an electric furnace in slight excess of that necessary to reduce the FeO. This operation yielded a metal high in iron and low in chromium and a beneficiated ore. A portion of the metal was to have been treated to yield a high iron ferrochrome-silicon to be added with the beneficiated ore to a third electric furnace. The latter operation would yield a low-carbon ferrochrome.

With small-scale tests on an ore of chromium-iron ratio 1.76:1 and a Cr$_2$O$_3$ content of 40 per cent, a product was obtained having a chromium-iron ratio exceeding 5:1 and containing 43 per cent Cr$_2$O$_3$.

In another method the ore underwent a direct and complete reduction with coke to yield a slag of the gangue constituents and a high-iron metal. A portion of this metal was selectively oxidized by the addition of chromite ore and lime. The chromium was selectively oxidized to Cr$_2$O$_3$, and the metal was left low in chromium. The remainder of the original metal was to have been smelted with silicon and coke to produce a ferrochrome-silicon low in carbon. This ferro alloy and the beneficiated ore were to be smelted to produce a low-carbon ferrochrome.

At the time of publication of this paper in 1938
only the initial reductions in these two processes had been attempted.

It was pointed out on page 2 that ferrochrome must be sufficiently high in chromium to not excessively chill the steel bath when added. A solution to this problem which permitted the use of high-iron ores was announced in 1941 by the Chromium Mining and Smelting Corporation. The constituents of the product developed were involved in an exothermic reaction when added to the furnace. The heat liberated more than compensated for the bulk of cold material. This process entailed the reduction of ore or concentrate with coke in an electric furnace to yield a chromium-iron metal of 8 to 10 per cent carbon and up to 5 per cent silicon. (This was possibly the first step of the selective oxidation process published in the paper three years previously.)

The product fed to the steel furnace consisted of this metal in a finely divided state mixed with sodium nitrate or other oxidizing agent in sufficient quantity to oxidize practically all the silicon and part of the carbon. The mixture was briquetted and heated, the oxidizing agent forming the bond. When the briquettes were added to the steel furnace, a molten ferrochrome containing about 6 per cent carbon and a slag of sodium silicate were formed.
Udy also described a low-carbon product which was made by oxidizing the above chromium-iron metal in the presence of lime at a high temperature to form a chemical combination of the oxides of lime and chromium. A mixture of these oxides and silicon, or a low carbon ferrosilicon, was ground to minus 100 mesh and bagged or briquetted and heated. Silicon was present in about 10 per cent excess over that required to reduce the iron and chromium. The carbon content was stated to be of the order of 0.02 per cent. A slag of calcium silicate forms in the bath as molten ferrochrome is liberated.

A recent review(13) of the actual application of these products in the manufacture of chromium steels indicates that they are highly successful in some operations and may even be used in making high alloy steels.

This chapter has presented several methods of attack on the problem all entailing a treatment of the entire volume of low-grade material. However, a process having numerous advantages would be one in which a rather small portion of the concentrate would be diverted and treated to yield a product with an extremely high chromium-iron ratio. This material would then be returned to the main body of the concentrate giving it a chromium-iron ratio equivalent to that of a high-grade ore.
CHAPTER III

EXPERIMENTAL METHODS

This chapter includes a discussion of the physical properties, chemical constitution, and methods of analysis of the concentrate. The induction furnace and accompanying converter are described. Pertinent data on refractories and slags are included with the method of procedure in the tests.

The Concentrate

The concentrate used in these experiments was from the Benbow property in the Stillwater district. The ore contained 22 per cent Cr\(_2\)O\(_3\). The ratio of concentration was approximately 2:1.

A preliminary screen analysis was obtained to gain a better understanding of the concentrate. With standard mesh screens the size distribution was as follows:

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Weight Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>+35</td>
<td>0.03</td>
</tr>
<tr>
<td>+48</td>
<td>6.43</td>
</tr>
<tr>
<td>+65</td>
<td>21.40</td>
</tr>
</tbody>
</table>
Mesh Weight Per Cent
+100  -65  21.04
+150  -100 16.80
+200  -150 13.16
-200  21.14

100.00

The presence of the greater part of the gangue in the finer sized fractions was to be expected of a table concentrate.

The mineral chromite is a member of the spinel group having the general formula R0·R2O3. The ideal chromite molecule is FeO·Cr2O3. In high-grade chromite ores FeO is largely replaced by MgO. The sesquioxide is mainly Cr2O3, but it may be replaced by Al2O3 and Fe2O3. It is interesting to note that ideal chromite has a chromium-iron ratio of 1.86:1 and has 68 per cent Cr2O3. A complete reduction would yield a ferrochrome with 65 per cent Cr. Despite the high Cr2O3 content, it would require some special treatment in order to yield a standard ferrochrome.

If a commercially acceptable alloy were to be the ultimate product of treating the concentrate, the problem was clearly one of removing a sufficient quantity of iron to increase the chromium-iron ratio to at least 2.5:1. By gravity concentration a considerable amount of iron
was removed in the gangue minerals—mainly silicates of iron and magnesium. In producing ferrochrome it is desirable to keep the quantities of $\text{Al}_2\text{O}_3$, $\text{MgO}$, and $\text{SiO}_2$ as low as possible; the greater the quantity of slag, the greater is the loss of chromium as $\text{Cr}_2\text{O}_3$.\(^{(22)}\)

Furthermore, the concentration step decreases the quantity of material to be handled and heated in all subsequent operations. The bond between mineral chromite and the gangue being comparatively weak, gravity concentration is highly successful.

There can, of course, be no mechanical separation of the $\text{MgO}$ and $\text{Al}_2\text{O}_3$ included in the chromite molecule. Apparently, a pyrometallurgical operation entailing reduction, partial (selective) reduction, or molecular replacement was the only solution to the problem if standard ferrochrome were to be the ultimate product whereby chromium could be admitted to steel.

A series of analyses for the chromium, iron, and aluminum on the concentrate yielded the following results. The magnesia, lime, and silica were approximate being taken from a composite analysis of the lot from which the working sample was obtained.
TABLE III

CHEMICAL ANALYSIS OF CONCENTRATE

Weight Per Cent

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_2$O$_3$</td>
<td>43.15</td>
</tr>
<tr>
<td>FeO</td>
<td>25.7</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>14.0</td>
</tr>
<tr>
<td>MgO</td>
<td>12.2</td>
</tr>
<tr>
<td>CaO</td>
<td>1.6</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

The lime, silica and probably part of the iron, alumina, and magnesia represented the included gangue. As previously stated, the concentrate had a chromium-iron ratio of 1.47:1. All iron in the chromite was assumed to exist as FeO. The portion, if any, existing as Fe$_2$O$_3$ was neither known nor determined.

Methods of Analysis

Considerable preliminary work was performed in obtaining an accurate determination of the Cr$_2$O$_3$ and FeO content of the concentrate. Although Low(11) and Keffer(8) were consulted and considerable useful information derived therefrom, Scott(19) presented details of manipulation which gave more consistent
results. The Cr$_2$O$_3$ and FeO of the concentrate and slags were ascertained in a similar manner. In fusing for Al$_2$O$_3$ determinations a nickel crucible was used.

A half-gram charge of pulverized material was placed in a crucible and fused with sodium peroxide. When this step was completed and the fusion cooled, the crucible and contents were placed in water to dissolve the chromates. Ferric hydroxide was removed by filtration.

The chromate solution was acidified and diluted, and aliquot portions were taken for titration. A few drops of diphenylamine indicator and an excess of standard ferrous ammonium sulphate solution were added. This excess was back titrated with an equivalent potassium dichromate solution.

The iron residue was dissolved in 1:1 hydrochloric acid and heated. Iron was reduced by boiling with test lead. The colorless ferrous iron solution was decanted from the lead and cooled. To the diluted solution 15 cubic centimeters of phosphoric acid restraining solution, three drops of diphenylamine indicator, and the standard potassium dichromate solution were added. By the use of diphenylamine a rapid titration and sharp end point were obtainable. This succinctly described method gave consistent results on the concentrate and some slags.
The complete dissolution of a sample of the ferrochrome produced in the smelting could not be obtained by the action of hot nitric, sulphuric, or hydrochloric acids, or various combinations of these acids. A successful fusion was not obtainable with sodium peroxide.

Dissolution was obtained with hot phosphoric acid, but considerable difficulty was encountered in attempting to get chromates from the chromus salts. A combination of hydrochloric and perchloric acids proved to be the best solvent; however, results were erratic and undoubtedly low.

The Induction Furnace

The furnace used in carrying out these investigations was a two pound, high-frequency induction furnace.

The three kilowatt converter supplying the high-frequency current operates from a single phase, 220 volt, 60 cycle line. It consists of a 35 ampere circuit breaker, a transformer, a spark gap, and a capacitor. The transformer charges the condenser to a high voltage (4400 volts on secondary) which discharges through the spark gap and furnace coils to generate electrical oscillations. The current may reach a value of 80 amperes or more in the frequency range of 30,000 to 50,000 cycles. Large currents are induced in the
conducting charge or crucible. By varying the spark gap in the converter the power to the furnace is regulated. All converter equipment is enclosed in a steel encasement measuring 37 inches high, 32 inches long, and 18 inches wide. Transformer, spark gap, and capacitor are water cooled.

The two pound induction furnace is simply a coil of copper tubing the ends of which are connected to the converter. The maximum permissible temperature of the cooling water flowing from the tubing is 80°C. The coil is mounted on a refractory base and frame. Liners of sheet mica adjacent to the coil allow the use of powdered insulators. Norsil, a pulverized silica, was used exclusively for this purpose. Temperatures of 2500°C are obtainable in this furnace.

With such furnaces the motor effect assures complete mixing of the molten metal thereby effecting complete reaction and rapid smelting. As with other types of electric furnaces, close control can be maintained.

Norbide (flaked graphite) crucibles were used in some of these investigations. Normalith, a water plastic material, was used to top the powdered insulator around the rim of the crucible. It was determined to be a chrome refractory.
FIG. I

Ajax-Northrup Two Pound
Induction Furnace

( 5 1/4 inch base)
Procedure of Tests

The general procedure in making test smelts consisted simply of adding to the heated furnace a given quantity of the concentrate and coke with varying amounts of fluxing agents. A balanced charge would ultimately yield a high-iron metal and a slag containing a sufficiently large portion of the chromium to permit its being separated from the metal and subsequently treated by one of two methods:

1. Reduce the chromium and iron to a standard ferrochrome by the addition of more coke and subjecting the slag to further smelting.

2. If a sufficiently large portion of the iron can be reduced in the first step without too great a slag loss of chromium, add the high-chromium low-iron slag to that quantity of raw concentrate which would yield a product with the effective properties of a high-grade chromite ore.

For preliminary tests to determine the character of the chromite at high temperatures, only coke was added in the charge. Theoretically, 4.28 parts of carbon would be required per 100 parts of the concentrate to reduce only the iron and form carbon monoxide. However, allowing for impurities in the coke and that carbon which would inevitably form iron carbides and chromium carbides together
with mechanical losses, 10 parts of coke were added per 100 parts of concentrate in the earlier tests.

As the slag was to be the economic product of the smelt, the matter of obtaining a slag with the desired characteristics was of major importance. The ideal slag would be one having:

1. A low temperature of formation to avoid excessive power requirements and other disadvantages accompanying higher temperatures.

2. A sufficiently low specific gravity to allow a quick and complete separation from the metal.

3. High fluidity to insure thorough mixing of reactants, aid in a rapid separation from the metal, and to facilitate pouring.

4. No constituent that would interfere with its subsequent treatment.

The extreme refractory character of chromite was the basis of the major difficulties encountered in the tests. The melting points of the pure constituents in the concentrate are given approximately as follows:
TABLE IV

MELTING POINTS OF PURE OXIDES IN CONCENTRATE

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Weight Per Cent</th>
<th>M. P. of Pure Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>43.15</td>
<td>2300°C</td>
</tr>
<tr>
<td>FeO</td>
<td>25.7</td>
<td>1420°C</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.0</td>
<td>2050°C</td>
</tr>
<tr>
<td>MgO</td>
<td>12.2</td>
<td>2800°C</td>
</tr>
<tr>
<td>CaO</td>
<td>1.6</td>
<td>2520°C</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.35</td>
<td>1750°C</td>
</tr>
<tr>
<td><strong>100.00</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As iron was desired to be removed as completely as possible from the slag, FeO could not be relied upon to lower the melting point. All other constituents have a melting point in the pure state approaching or greatly exceeding 2000°C. Of those constituents to be slagged Cr₂O₃, Al₂O₃, and MgO made up the bulk.

The ternary equilibrium diagram Cr₂O₃-Al₂O₃-MgO would have been a direct aid in the solution of the slag problem; however, none could be found in the literature.

From a study of the accompanying ternary equilibrium diagram Fig. 2, (5) CaO-Al₂O₃-MgO, it was apparent that a melt of pure Al₂O₃ and MgO in the proportions of the concentrate would have a melting point of approximately
Equilibrium Diagram of the System CaO-MgO-Al₂O₃

Pt Crystal Phases Temp
1 MgO-CaO-3CaO·Al₂O₃ 1450°
2* MgO-3CaO·Al₂O₃-5CaO·3Al₂O₃ 1345°
3* MgO-5CaO·3Al₂O₃-1CaO·Al₂O₃ 1345°
4 MgO-MgO·Al₂O₃-2CaO·Al₂O₃ 1370°
5 MgO·Al₂O₃-CaO·Al₂O₃-3CaO·5Al₂O₃ 1550°
6 MgO·Al₂O₃-3CaO·5Al₂O₃-Al₂O₃ 1680°

* Eutectic

FIG. 2

KEUFFEL & ESSER CO., N.Y. NO. 3444A
TRIANGULAR CO-ORDINATE
PATERSON, N.J.
2050°C. From the curve in Fig. 3(5,6) it was observed that a melt of Cr$_2$O$_3$ and Al$_2$O$_3$ in the molecular ratio in which they exist in the concentrate would have a melting point of 2280°C. Similarly, the Cr$_2$O$_3$-MgO curve indicated a melting point of 2400°C for a melt of these two oxides existing in the same molecular proportions as they did in the concentrate. The eutectic composition of these three constituents would accordingly have a much lower melting point.

As it was intended to ascertain the effect of adding lime upon recovery of Cr$_2$O$_3$ by replacement of FeO by CaO, reference was made to Fig. 2 and Fig. 3 that a knowledge of its slagging effect might also be gained.

Considering a modification of Fig. 2 wherein Cr$_2$O$_3$ is added to the Al$_2$O$_3$-MgO binary system in a constant amount equal to that fraction of the total Cr$_2$O$_3$, Al$_2$O$_3$, and MgO which it occupies in the concentrate, some generalizations may be drawn. Of the total of these three oxides 62.2 per cent is Cr$_2$O$_3$, 20.2 per cent is Al$_2$O$_3$, and 17.6 per cent is MgO. Of the total Al$_2$O$_3$ and MgO, 53.5 per cent is Al$_2$O$_3$.

The modified ternary diagram would have pure CaO for one corner, 37.8 per cent MgO-62.2 per cent Cr$_2$O$_3$ replacing the MgO corner, and 37.8 per cent Al$_2$O$_3$- 62.2 per cent Cr$_2$O$_3$ replacing the Al$_2$O$_3$ corner. The composition
Molecular per cent $\text{Cr}_2\text{O}_3$

Melting Curves of $\text{Cr}_2\text{O}_3$ with $\text{MgO}$, $\text{Al}_2\text{O}_3$, and $\text{CaO}$

FIG. 3
representing the concentrate without the iron would remain on the MgO-Al₂O₃ line at 53.5 per cent Al₂O₃.

Referring again to Fig. 3, it was observed that a melt of 37.8 per cent MgO-62.2 per cent Cr₂O₃ would have a melting point of 2450°C at 30.2 molecular per cent Cr₂O₃. A melt of 37.8 per cent Al₂O₃-62.2 per cent Cr₂O₃ would have a melting point of 2250°C at 52.5 molecular per cent Cr₂O₃. As 2800°C is the melting point of MgO and 2050°C is the melting point of Al₂O₃, it would not be unreasonable to assume the eutectic composition of the modified ternary system to be much nearer the center of the field than that of the simple CaO-MgO-Al₂O₃ system as drawn. If this is true, then the addition of lime in a quantity to be experimentally determined would render a slag having a composition closely approaching that of the eutectic and accordingly one with the lowest melting point.

These observations and generalizations were made purely in an attempt to arrive at a slag with a low temperature of formation and a low melting point. The effect of lime upon the direction and degree of completion of reactions occurring and the effect of this flux upon the selection of a crucible which would meet all requirements were factors of as great importance as the melting point of the slag.
The temperatures required in smelting such a refractory substance as chromite seriously limit the number of materials of which a suitable crucible may be made. In applying an induction furnace to the smelting of chromite or any non-conduction material, it was necessary to have within or surrounding the charge an electrical conductor as a source of the necessary heat. A choice of such conductors is limited to only a few materials. The stability of graphite at the temperatures employed, its good electrical conductivity, and its low cost have brought about its wide application to almost all types of electric furnaces. However, if a graphite crucible were used, controlled selective reduction would have been impossible; the charge would attack the crucible and, more important, chromium would be excessively reduced.

The only alternative was to place an inert refractory lining in the graphite crucible. With such a setup, until metal formed, all heat delivered to the charge passed through the refractory lining. Even the reduced metal conducted only a portion of the current, and the outcome was the application of intense heat on both sides of the lining.

It would have been desirable to have had a refractory lining of high thermal conductivity. However,
this property was secondary to the absolutely essential requirements of infusibility and the resistance to the corrosive action of slag or metal.

Although it may have been possible to produce a slag with a very low melting point, the minimum temperature of smelting was determined by the melting point of the metal which would approximate 1500°C (14) for the low-chromium iron desired.

Alundum crucibles, although having a melting point of approximately 2050°C (18), had not the required resistance to the molten charge.

Magnesia is stated (18) to have a melting point of 2800°C. It is a good conductor of heat, and when hot becomes a fairly good conductor of electricity. (12) These properties would tend to make magnesia desirable. The mechanical weakness of magnesia at high temperatures would not constitute too serious a problem in the small furnace. Electric furnaces producing ferrochrome are lined with magnesite. (1)

This chapter has dealt with the properties of the concentrate and the equipment and experimental procedure required in treating the concentrate as a result of these properties.
CHAPTER IV

EXPERIMENTAL RESULTS

Included in this chapter is a sequence of the experiments with descriptions of the charges, conditions of smelting, and results obtained.

For the earlier tests it was decided to use a charge of 120 grams of concentrate and 12 grams of coke and to observe the reaction of this combination in this proportion. In a preliminary attempt it was found that considerable fine coke was lost in the evolved carbon monoxide. Thereafter, screened coke was utilized.

Smelt One

The extent to which the graphite crucible would be attacked by the oxidizing slag and the metal was not known. For the first smelt a Norbide crucible was used. It measured 2 7/8 inches high, 2 5/8 inches in diameter, and the wall was 3/8 inch thick. A charge consisting of 120 grams of chromite concentrate and 12 grams of minus 28 mesh plus 80 mesh coke was added when the crucible became red.

A small brick was placed over the furnace throughout all operations to maintain a reducing atmosphere and prevent chilling of the charge. As reduction proceeded considerable quantities of carbon monoxide were evolved.
and ignited in the air. At no time during these experiments was metal produced in quantities below an extremely white heat.

After twenty-five minutes, reduction appeared complete, and the contents were poured. Ordinary assay crucibles were used to receive all melts. The Norbide crucible was pitted and eroded below the slag line to depths of approximately 1/8 inch.

The metal did not pour into one globule but was dispersed in the slag. When cool the metal and slag were crushed and the larger pieces of metal removed by hand. The separation of the fines was easily brought about with a magnet; the slag was only weakly magnetic. Metal produced in this smelt was extremely hard.

The metal weighed 32.7 grams; the slag, 79.7 grams. The slag was 33.3 per cent Cr₂O₃ and 20.2 per cent FeO indicating a chromium-iron ratio of 1.43:1 which was somewhat less than that of the concentrate. Of the chromium in the charge 51.4 per cent was in the slag. Of the iron in the charge 53.1 per cent was in the slag. This indicated a simultaneous reduction of Cr₂O₃ and FeO.

By difference, the reduced chromium and iron gave up considerably more oxygen than could possibly have been removed by the 12 grams of coke.

Obviously, selective reduction could not have been
accomplished while the charge was in contact with the graphite crucible. From the quantity of chromium reduced it appeared that a limited amount of coke would not selectively reduce the iron unless the slag composition were altered. Of these two problems—the crucible lining and the slag—the former was of primary importance; a properly balanced slag would be of no avail without a suitable crucible lining.

An attempt was made to line the Norbide crucible with powdered magnesia using a small amount of water glass as a binder. The lining was dried slowly and then heated slowly. As cracks developed, they were patched, and the lining again dried and heated. At a red heat the lining warped. Because magnesia is non-plastic and requires a binder which could withstand the severe conditions of the chromite smelt and because such a lining would undoubtedly require a press before firing, the attempt at lining the Norbide crucible was temporarily abandoned.

The section of the furnace in Fig. 4 shows the setup for melting metals. Around the alundum crucible is packed the powdered silica, Norsil. Between this insulator and the coil are three layers of mica sheet. Around the rim of the crucible is a ring of the plastic chrome refractory, Normolith. Cooling water and converter leads are shown.
Smelt Two

In a second attempt graphite electrode scrap was ground to minus 1/4 inch and was packed around an alundum crucible replacing the Norsil in the above setup. Four mica sheets were used between the graphite and the coil.

The interior of the crucible came to a dull red heat. Cooling water entering the coil was at 5°C, and that leaving the coil was at 29°C. These two temperatures remained constant throughout the test.

A charge of 120 grams of concentrate and 12 grams of coke was added. After an hour apparently no reduction had occurred. The quantity of water leaving the coil per minute was measured, and from the 24°C rise in temperature power loss was calculated to be 2 kilowatts. Two thirds of the power delivered to the furnace was being lost due to poor insulation. When cool the charge was examined and was found to be unaffected.

Smelt Three

In another attempt to ascertain the outcome of a reduction with 10 parts of coke to 100 parts of concentrate an ordinary assay crucible was placed in a 12 kilowatt Hoskins Electric Furnace. When at a red heat 120 grams of concentrate and 12 grams of coke were added to
Ajax-Northrup
Two Pound
Induction Furnace

Scale: $\frac{3}{4}'' = 1''$

FIG. 4
the crucible. The furnace was maintained for one hour at its maximum temperature which was probably no more than 1500°C. After removal several small globules of metal were scattered throughout the sintered charge.

Smelt Four

Two layers of asbestos were placed inside the mica sheets of the induction furnace. Ground graphite electrode was again placed around the alundum crucible. A sequence was followed similar to that in the second smelt. This time, however, the crucible was somewhat hotter than before. Nevertheless, when the temperature rise and rate of flow of the cooling water were measured 1.26 kilowatts were found to be lost due to insufficient insulation. After an hour the charge was unaltered.

Smelt Five

An attempt was made to line the Norbide crucible with Normolith. Although this refractory had at no time softened when in contact with the graphite during other heats, it was questionable that the binding agent rendering it plastic would withstand the temperatures in the crucible.

A 3/16 inch lining was moulded in the Norbide crucible. Norsil being packed around the crucible, there
was little heat loss in the cooling water. After thirty minutes the temperature was still below that required to smelt the chromite. The lining softened and cracks developed. At a white heat the charge sintered, but the Normolith on the crucible walls above the charge became very soft and collapsed.

The cooled sinter was a mixture of Normolith and chromite. However, several small beads of metal were present.

**Smelt Six**

The setup of the alundum crucible with ground graphite packed around it failed from an insufficient insulation. A smaller alundum crucible allowing ample room for both graphite and Norsil was obtained. The thimble was 3 3/8 inches high and only 1 5/16 inches in diameter. This thimble was placed in a can measuring 2 1/4 inches in diameter. Graphite bound with tar was packed around the thimble, and the unit was baked. The can was removed, and the unit was baked again. All volatile substances were vaporized. The unit failed to heat in the furnace, however.

Fig. 5 is a general view of the converter, furnace, and several of the crucibles used in these test smelts. On the front of the converter is the switch and spark gap
FIG. 5

Converter, Furnace, and Crucibles
control. In order to the right of the furnace are the Norbide crucible, alundum crucible, can used in the sixth smelt attempt, alundum thimble, machined graphite electrode which was used in smelts seven and eight, and a fire clay crucible for receiving the melts.

Smelt Seven

Graphite electrode connecting pins were machined to a size that would permit ample insulation and contain the alundum thimble. These graphite crucibles were 2 1/4 inches in diameter with walls 3/8 inch thick.

When the empty thimble was heated for 20 minutes, it became white hot. A charge of 60 grams of concentrate, 6 grams of coke, and 12.6 grams of lime was then added. Reduction began at a white heat, and forty minutes later, when carbon monoxide ceased to be evolved, the melt was poured. All but the rim of the crucible had been fluxed and was in the slag. The graphite had been severely corroded.

Due undoubtedly to the lime present the slag was very fluid. In the previous smelts where equal temperatures were attained the slag was somewhat viscous.

The slag weighed 43.31 grams, and the metal, 18.175. The metal contained grey oriented needles, was brittle, was non-magnetic, and was very porous. According to Keeney(12) ferrochrome displaying such properties
contains 7.5 to 9 per cent carbon.

Reasonable and consistent results could not be obtained in analyzing for the chromium and iron in the slag and metal.

Smelt Eight

A furnace setup like that of the seventh smelt was again used. The empty thimble was heated to the temperature 1650°C as indicated by an optical pyrometer. At 1725°C the alundum thimble softened and while doing so the temperature dropped.

The power was turned off till the furnace had cooled to a red heat. A charge of 40 grams of concentrate, 4 grams of coke, 28 grams of lime, and 0.5 grams of fluorite was then added. In an attempt to effect a smelt without injuring the thimble, the temperature was kept down. Nevertheless, when, after forty-five minutes, the reduction was complete and the melt was poured, all but the rim of the thimble had again been slagged. The melt had been in contact with the machined graphite crucible.

The metal and slag closely resembled those of the previous smelt. It was evident from the quantity of the metal and the eroded condition of the graphite crucible that a large portion of the chromium had been reduced.
Summary

The original purpose of this work was to determine by laboratory means whether a high-iron chromite concentrate were amenable to a pyrometallurgical treatment comprising a selective reduction of a portion of the iron and the consequent production of a low-iron slag which upon further treatment would yield a standard grade ferrochrome.

The results of experiments herein described are not sufficient in quantity or variation to allow a definite relationship to be found between the proportion of coke and fluxes to concentrate which would yield a successful smelt. Such results would be dependent upon the tests being conducted in inert surroundings permitting a controlled charge.

The primary problem, therefore, became one of procuring a suitable lining for the graphite crucible. A review of refractories indicated that a magnesia crucible would be capable of withstanding the severe conditions of temperature and corrosion.

The machined graphite electrode was very satisfactory from the standpoint of temperatures attainable, and its
ability to be machined to comparatively wide limits in size to accommodate a given crucible greatly increases its value.

A very notable increase in the fluidity of the slags for the seventh and eight smelts in which lime was used favored its use as a flux. No great difference was apparent between the two although a much greater proportion of lime was used in the latter. The effect of lime on the efficiency of selective reduction could not, of course, be ascertained.

Conclusions

It is the belief of the investigator that the execution of this work has been a real contribution to a solution of the problem of successfully treating our domestic high-iron chromite ores.

The induction furnace applied in the investigation has introduced the refractory problem, yet, if the problem can be overcome, this type of furnace will become ideal for such work on non-conducting charges.

Recommendations

Magnesia crucibles of the proportions required by the furnace have not been available during this work. In the event that a magnesia or other lining will allow
the performing of the type of experiments originally outlined, the investigator suggests a course of tests including a determination of the effect of the speed of reaction on the recovery of chromium.

In all smelting attempts the concentrate was charged as received. When furnace conditions make such tests possible, knowledge should be gained of the effect of further grinding the concentrate on the speed of reaction and the consequent effect on the recovery of chromium.

The effect of increased slag volume on the recovery of chromium is a variable to which attention is due.

A study of oxide melts similar to that included here would be an early aid in the slag problem.
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