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of
MONTANA CHROMITE

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A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
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INTRODUCTION

In 1939 the total world production of crude chromite was approximately 1,167,000 metric tons,[1] of which the United States produced only 3,672 metric tons and imported over 317,500 metric tons. Imports came mostly from the Philippine Islands, Cuba, South Africa, and Rhodesia.

There are large domestic deposits of low grade chromite in California, Oregon, Wyoming, and Montana which have hardly been touched since the first World War. In 1918, the United States produced over 79,000 long tons[7] of chrome ore. Of this total 56,200 long tons came from California, 22,500 from Oregon, and the remainder from Maryland, North Carolina, Pennsylvania, Washington, and Wyoming. No shipments of chromite were reported from Montana, although some mining claims were filed upon in this state in Stillwater, Sweetgrass, and Park counties, and some chrome ore was highgraded at that time.

This 1918 output was much larger than that of the previous year, and if the demands and high prices created by the war had continued, the total production of crude ore in 1918 would probably have been nearly 100,000 long tons,[7] an amount believed to be approximately equal to the United States chromite consumption for that year. When the Armistice was signed in 1918, many new owners of chrome ore deposits were preparing to put chrome ore on the Pacific

* Numbers refer to bibliography on page 40.

Coast market. But with the lowering of import duties on foreign ore, the domestic producers ceased operations almost completely and have remained idle until very recent years.

Recent developments[8] in the domestic chromite industry include the following: (a) The Grey Eagle mill in Glen County, California started operations in March, 1942 at the rate of 15,000 tons of metallurgical grade concentrates per annum. (b) Arrangements have been made in California and Oregon for purchase of chrome ores in small ton lots from numerous small operators. (c) In Montana, one mill went into operation on the Benbow property in Stillwater county at the rate of 60,000 short tons of concentrates per annum, and plans are under way for increasing the present capacity by 150 per cent before the end of 1942. Another mill is expected to be in operation before the end of this year on a basis of 150,000 tons of concentrates per annum. Still another property is expected to be in production at the rate of 60,000 tons per annum by the end of 1942. Thus, at the close of this year the production rate of Montana alone is expected to be over 360,000 short tons per annum. (d) In Oregon a mill for recovering chromite from bench gravels is well under way with a contract to deliver 30,000 tons of chromite per annum. (e) And in Wyoming arrangements have been made for the production of 35,000 tons of concentrates per annum.

In view of the fact that we have these large domestic

deposits of chromite, which is a very essential peacetime as well as wartime mineral, metallurgical processes should have been developed long before for their treatment. The domestic concentrates being produced at the present time are sweetened with imported ore having a higher Cr:Fe ratio before being smelted to ferrochrome.

The pure chromite molecule consists of iron oxide and chromium oxide in the formula $FeO.Cr_2O_3$. In naturally occurring deposits, the iron may be partially replaced by magnesium and the chromium by aluminum and iron giving the molecule $(Fe,Mg)O.(Cr,Al,Fe)_2O_3$. The chief difference between the domestic chromite and that imported is that the latter has more of the iron replaced by magnesium, thereby giving a higher Cr:Fe ratio than that of the domestic chrome ores. High grade imported metallurgical ore has a Cr:Fe ratio of over 2.5, whereas the domestic concentrates seldom run higher than 1.7. A direct smelt of the ore or concentrates will yield a ferrochromium of approximately the same Cr:Fe ratio as the original product. Therefore, since the steel manufacturers base their metallurgical practices upon a high Cr:Fe ratio ferrochromium, the removal of a part of the iron in the domestic product is of prime importance at the present time. Of course, if the importing of foreign ores is completely stopped before new metallurgical processes are developed to handle the domestic concentrates, the steel industry will have to use the domestic product, producing chromium steels at a higher cost and at a slower rate.

The purpose of the investigations presented herein is twofold: first, to determine the best slag for a direct smelt of the domestic concentrates; and second, to try to discover a suitable refractory crucible for an induction furnace which will withstand very high temperatures and at the same time not react with the charge of chromite and fluxes.

PREVIOUS INVESTIGATIONS

For over three years previous to 1938, Marvin J. Udy[5] of the Chromium Mining and Smelting Corporation of Canada operated an experimental plant at Sault Ste. Marie, Ontario for the express purpose of developing metallurgical processes for the treatment of domestic chrome ores of the United States and Canada, and particularly of the deposits at Obonga lake, near Collins, Ontario.

Taking advantage of the fact that the Cr_2O_3 part of the chromite molecule has a higher heat of formation (267,500[10]cal./gr.) than the FeO part (64,000[10]cal./gr.), both selective reduction of the iron and selective oxidation of the chromium were tried.

The basic principle of the selective reduction process is to convert the more easily reducible FeO to metallic Fe and replace the FeO removed from the chromite molecule with CaO, at the same time keeping the Cr_2O_3 in oxidized form. Only enough iron is reduced to bring the Cr:Fe ratio in the chromite up to required standards.

The resulting "beneficiated ore", which is essentially a basic chromite, is smelted with silicon, ferrosilicon, or high silicon ferrochromium to flux off the CaO and give a low carbon ferrochrome ready for market. Figure 1 shows a flowsheet of this selective reduction process.

In selective oxidation, both the FeO and the Cr_2O_3 are first reduced with coke to a high carbon chrome-iron metal. Then the Cr is oxidized to Cr_2O_3 with chrome ore and lime, while much of the iron remains reduced. The Cr_2O_3, which is removed in the slag, is termed "beneficiated ore." This is selectively reduced as before into a low carbon ferrochromium ready for market. Figure 2 shows a flowsheet of this process.

Since 1938, Udy[6] has developed two more chrome products from domestic chromite ores: (1) a high Cr:Fe ratio concentrate, and (2) Chrom-X, both high carbon and low carbon.

The concentrate with the high Cr:Fe ratio is made "either by fusing the ore or concentrates with lime and reducing the iron with part of the chromium, or by fusion of the ore with lime to replace the iron and part of the alumina from the chromite and then concentrating by water to remove the altered chromite of high Cr:Fe ratio." In the chromite molecule, $(Fe,Mg)O.(Cr, Al,Fe)_2O_3$, the iron is replaced to some extent by Mg and the Cr by Al and Fe. The ore also contains $xMgO.ySiO_2$. Udy's principle here is to add CaO which will replace the MgO from the silicate,

High Iron Chrome Ore
Cr:Fe below 3:1

lime and coke

Smelt in 3-Phase submerged-arc furnace

Metal
High in Fe
Low in Cr

Beneficiated ore (basic
chromite) Cr:Fe above 3.5:1

Si or FeSi

Discard as
By-product

Smelt in 3-phase sub-
merged-arc furnace to
ferro-Cr of high Si
and low C content

Smelt in
Heroult-type
furnace

Low C ferrochrome
70% Cr or better
for market

Slag to
waste
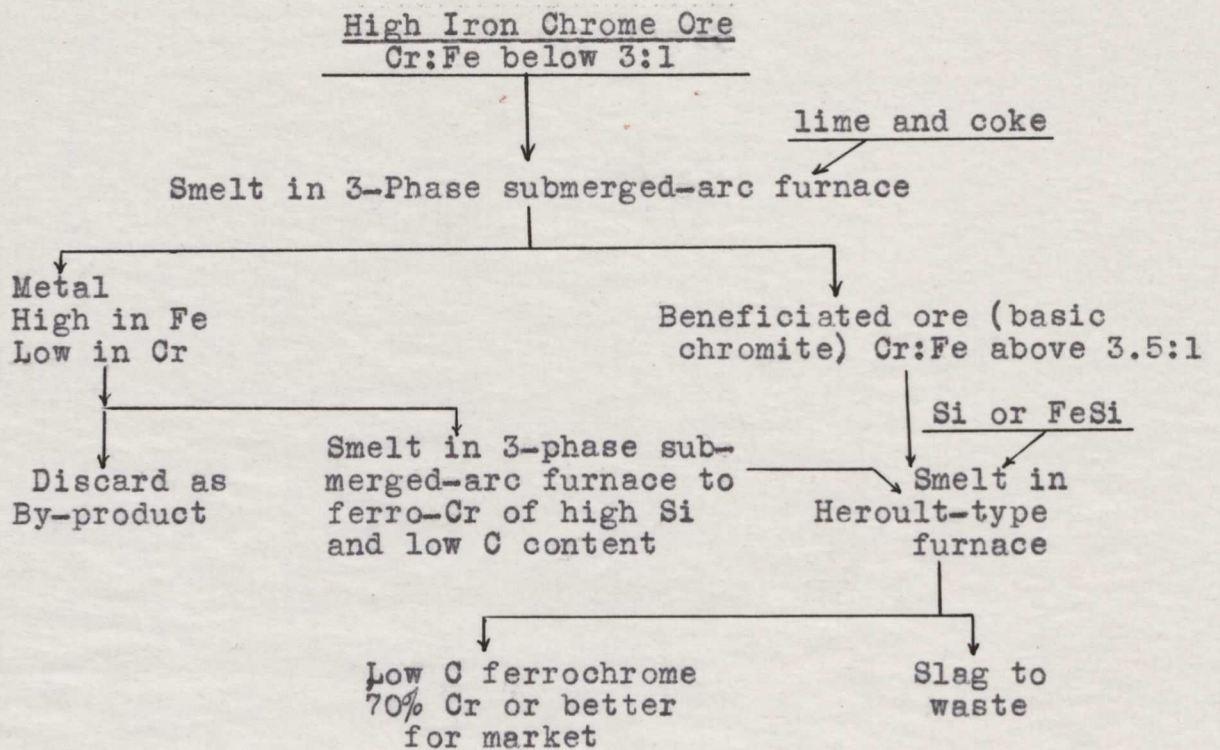
Figure 1 --- Flowsheet of Selective Reduction Process.

High Fe Chrome Ore
Cr:Fe below 3:1

Smelt in 3-phase submerged arc electric furnace

Slag to waste

Cr - Fe metal
8% C

Smelt in 3-phase submerged
arc furnace with Si and Coke
to produce Ferro-chrome-Si
low in C

Smelt in Heroult-
type furnace with
chrome ore and
lime.

Beneficiated ore

High-Fe, Low-Cr
by-product

Smelt in Heroult-type furnace

Slag to waste
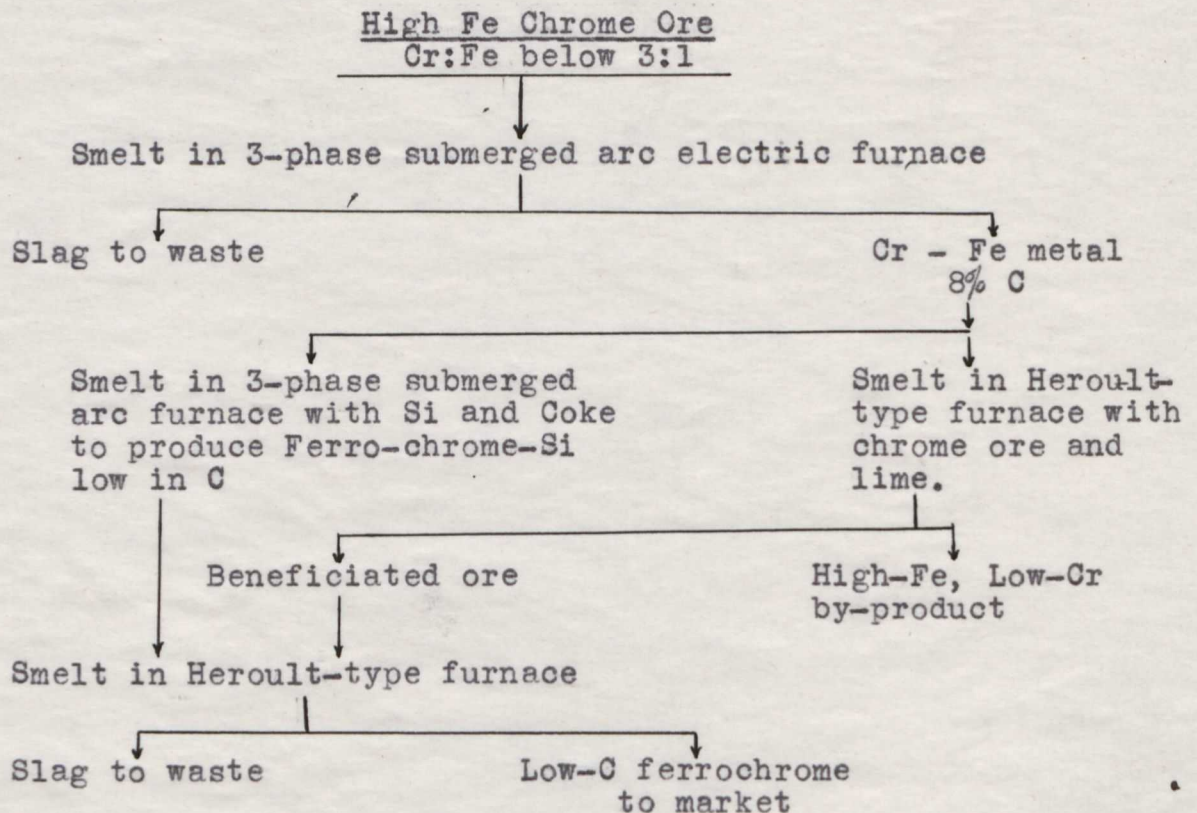
Low-C ferrochrome
to market

Figure 2 --- Flowsheet of Selective Oxidation Process.

the MgO in turn replacing the FeO in the chromite molecule. The resulting product, which approaches magnesium chromite ($MgO.Cr_2O_3$) in composition, crystallizes as an altered chromite and, according to Udy, can be easily se separated by water concentration. Then this product can be used to sweeten ore with a low Cr:Fe ratio.

In making high carbon Chrom-X, the ore or concentrates are smelted directly in an electric furnace to a chrome-iron metal containing 8 to 10 per cent carbon and up to 5 per cent silicon. To this metal an oxidizing agent such as $NaNO_3$ is added to give enough oxygen to oxidize practically all of the silicon and part of the carbon. The mixture of metal and oxidizing agent is ground up, briquetted, and put into bags. When added to the steel bath, it reacts to form a molten ferrochromium of about 6 per cent carbon content, and a fluid sodium silicate slag. Since the reaction is exothermic, it doesn't cool the bath.

In making low carbon Chrom-X, the ore or concentrates are first smelted directly to a high carbon chrome-iron metal. This metal is oxidized with lime at a high temperature, the operation being so controlled that about 50 per cent of the Cr oxidizes to Cr_2O_3 and 50 per cent to CrO_3. These ratios are varied to give the right amount of heat so that when the Chrom-X is added to the steel bath, it neither chills nor overheats the steel. Then the oxides of Cr and Fe, which are in chemical combination with the lime, are ground together with silicon or low carbon

ferrosilicon and bagged for shipment or briquetted into bricks. The silicon is present in about 10 per cent excess over that needed to completely reduce the oxides of iron and chromium. When added to the steel bath, this low carbon Chrom-X reacts to form a very low carbon ferrochromium and a calcium silicate slag.

John H. McDonald[11] superintendent of the open-hearth department of the Algoma Steel Corp., Ltd. of Sault Ste. Marie, Ontario, has conducted several experiments with Chrom-X in the manufacture of chromium steel. To date this company has used 1,250,000 pounds of high carbon Chrom-X, and most of the chromium steel manufactured is in service at the present time. McDonald states that, "The procedure used with Chrom-X is quite simple and requires no drastic change from the practice with ferrochromium." and that, "The recovery of chromium from ferrochromium averages 88 per cent while the figure for Chrom-X is 95 per cent." The Chrom-X is placed in the ladle and the molten steel is tapped into it.

The following is a summary of the work done by J. Koster[4] of the United States Bureau of Mines during 1936:

Several tests were run on concentrates from domestic chrome ores using a graphite crucible in a 35-kv-a induction furnace. The concentrates, which came from chromite of the Stillwater complex, analyzed 23.66 per cent FeO and 44.66 per cent Cr_2O_3. Several charges consisting of 500 grams chromite concentrates, 100 grams coal, 75 grams

sand, and 15 grams fluorspar, were smelted to determine the probable grade of ferrochromium that this domestic chromite would yield. Their best results with concentrates showed a Cr:Fe ratio of about 1.7:1 in the metal, with a 75 per cent recovery of Cr.

From experiments on the crude ore, Koster concluded that it is possible to produce ferrochromium in the ordinary way from crude Montana chromite with recoveries of over 80 per cent. Carbon content was 8 to 10 per cent.

Matte smelting of the chrome ore with pyrite was tried, resulting in a matte with a Cr:Fe ratio higher than that in the ore and a metal with a lower Cr:Fe ratio than that in the ore. After plotting the results on a Fe-Cr-S system, it was concluded that the nature of the system is such that it will be difficult to achieve good recoveries of the high-ratio matte.

Upon smelting a chrome-iron metal with copper, two layers were formed, a chrome layer and a copper layer. The results of several fusions were plotted on a ternary diagram. Since the line representing the chrome layer was parallel to the Fe-Cr side at a point about 2 to 4 per cent Cu, and the line representing the copper layer was parallel to the Fe-Cr base at a point averaging 93 to 95 per cent Cu, it was concluded that no separation of iron and chromium can be expected by smelting with copper to form a duplex system.

Smelting chromite in the presence of Cu_2S yielded a

matte having a splendid Cr:Fe ratio but containing considerable copper.

Experiments in decarburization of ferrochromium, made in the ordinary manner from Montana chromite, with metallic calcium showed that some of the carbon could be removed but that a great excess of calcium is required, at least on small batches.

Metallic silicon also removed some of the carbon, but the resulting metal was high in silicon.

An experiment was tried on the reduction of chromite in a small arc furnace using metallic silicon as the reducing agent. The ferrochromium produced contained 3.1 per cent carbon, most of which probably came from the coke required to start the arc. It was concluded that a larger furnace would be necessary for a successful experiment of this kind.

COMMERCIAL MANUFACTURE OF FERROCHROMIUM AND CHROMIUM

Ferrochromium is almost universally made in electric furnaces, usually of the open-top, three-phase, arc type. The high grade ore containing from 41 to 55 per cent Cr_2O_3 and from 13 to 22 per cent FeO^4 is mixed together with a reducer (usually anthracite coal), sand, fluorspar, and lime. This charge is fed into the top of the furnace around the electrodes, and more is added from time to time to keep a layer of unfused charge next to the electrodes. Chromite or magnesite refractory walls are used, and the electrodes are kept far enough away from the sides to allow

a layer of charge to freeze on them. The metal is tapped at about two-hour intervals, both slag and ferrochromium being drawn from the same tap hole. After cooling, the slag is broken away from the alloy. The ferrochromium produced in this manner will run from 4 to 10 per cent carbon, depending upon the amount of reducing agent in the charge.

Low carbon ferrochromium is produced by adding lime and chromite to this molten alloy to oxidize out the carbon. A high chromium slag is produced here which is reworked. Silicon or high silicon ferrosilicon may also be used as the reducing agent instead of carbon for the production of low carbon ferrochromium.

Metallic chromium may be produced by the reduction of Cr_2O_3 with aluminum according to the following reaction:

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3.$$
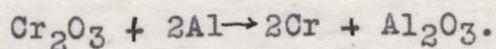
Silicon may be substituted for the aluminum in the above reaction. The Cr_2O_3 is obtained by a leaching and evaporation process on chromite concentrates which have been roasted with Na_2CO_3 and $CaCO_3$.

Metallic chromium may also be electroplated from solutions of chromium salts.

USES OF CHROMIUM

The largest use of chromium is as an alloying element in the steel industry. It is used in stainless steels, low chromium structural steels, armour plate, heat and

corrosion resistant alloys, abrasion resistant alloys, and many other important alloys.

Practically the only use of pure chromium is in electroplate. Here it has a brilliant luster when polished, is highly resistant to corrosion and abrasion, and is very hard.

Crude chromite ore or concentrates find several uses in industry as refractories, chiefly as linings for open-hearth steel furnaces. These refractories have good corrosion resistance and heat shock resistance.

Compounds of chromium are used in dyes, pigments, paints, the tanning industry, and in the manufacture of other chrome salts used for various purposes.

EXPERIMENTAL WORK

Furnace Used

A new Ajax-Northrup induction furnace, put out by the Ajax Electrothermic Corporation of Trenton, New Jersey, was used in this experimental work. It consists of two units, a 3 KW. converter, and the furnace itself. A schematic drawing of the circuit is shown in Figure 3.

The standard 3 KW. converter, operating from a 220 volt, 60 cycle, single phase line, is made up of a circuit breaker, transformer, spark gap, and capacitor. The transformer steps the voltage up to approximately 4400 volts, a potential high enough for effective spark gap operation, and charges the condenser of the capacitor to this high
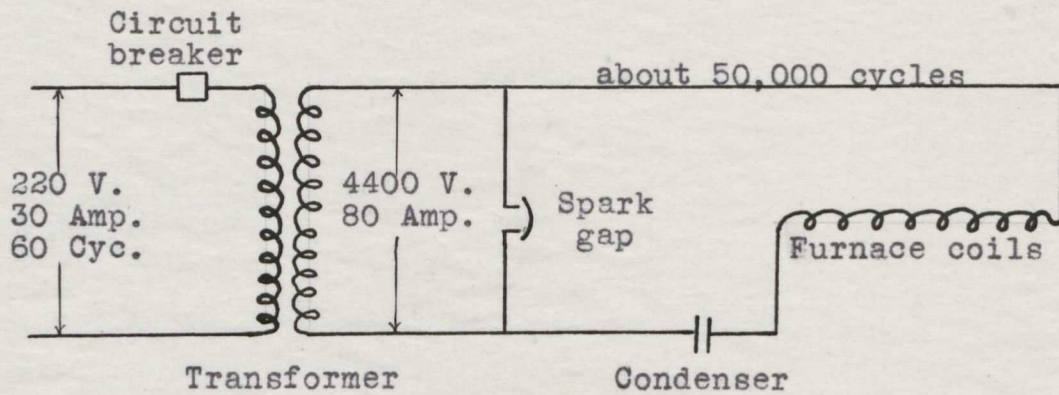
Figure 3 - Diagramatic Drawing of Converter
and Furnace Circuit.
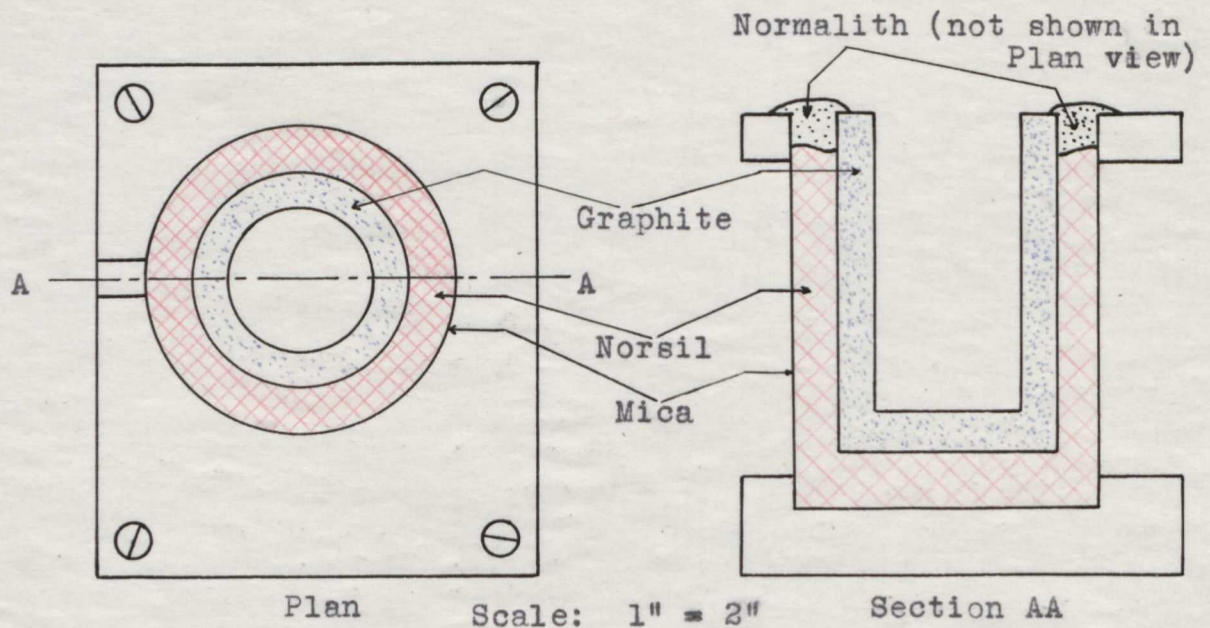
Figure 4 - Furnace with Standard Machined Graphite
Crucible. Coils are not shown.

voltage. The condenser in turn discharges through the spark gap which sets up electrical oscillations, changing the 60 cycle current to approximately 50,000 cycle current.

The furnace is merely a coil of copper wire surrounding an insulated crucible. The high-frequency current from the converter sets up an oscillatory electro-magnetic field inside the furnace coils. This field induces large electric currents in the conducting charge or crucible for heating it.

The capacitor, gap, transformer, and furnace coils are all cooled with water running from the tap. Outlet temperature of the water from the transformer should not exceed 30 degrees Centigrade, and that from the furnace coils should not exceed 80 degrees Centigrade.

Furnaces of 1/8, 1/2, 1, 2, and 4 pound capacities are available for use with the 3 KW. converter. The two-pound furnace, two views of which are shown in Figure 4, was used by the author.

Products used in connection with this furnace include: (a) sheets of natural mica to be put next to the coils for electrical insulation, (b) norsil, powdered silica, to be tamped around and under the crucibles for heat insulation, (c) norblack, a specially prepared lampblack, for heat insulation at higher temperatures, (d) fused silica tubes for electrical insulation next to the coils when norblack heat insulation is used, (e) normalith, a refractory cement, to be sealed around the top of the insulation, and

(f) crucibles of the following materials: graphite, alundum, magnesia, norbide, clay graphite, zirconium silicate, molded silica, and fused silica.

An old Hoskins electric resistance furnace made by the Hoskins Manufacturing Company of Detroit, Michigan was tried out, but the highest temperature attained would not melt the charge. Therefore, all the experimental work was carried out in the induction furnace described above.

Products Used

Several pounds of chromite concentrates were obtained from the Anaconda Copper Mining Company at Anaconda, Montana, where Benbow chromite from the eastern part of the Stillwater complex in Stillwater county, Montana had been concentrated in a pilot plant. Concentration was done in hydraulic classifiers, followed by tables and a differential density cone. A complete analysis of the concentrates given by the company was as follows:

$$FeO - 22.1 \% \qquad MgO - 15.5 \%$$
$$Cr_2O_3 - 43.0 \% \qquad SiO_2 - 3.35 \%$$
$$Al_2O_3 - 17.2 \% \qquad CaO - 1.60 \%$$
$$Cr:Fe = 1.83.$$

The author's analysis ran:

$$FeO - 27.0 \%$$
$$Cr_2O_3 - 43.8 \%$$
$$Cr:Fe = 1.52.$$

A screen analysis of the material, made by the author, is given on the following page:

Mesh	Per Cent		Mesh	Per Cent
+ 35	0.0		+ 150	15.8
+ 48	5.2		+ 200	13.5
+ 65	19.5		- 200	25.8
+100	20.2			

The sand used, which was assumed to be pure SiO_2, was all - 20 + 65 mesh material.

The coke analysed approximately 92 per cent carbon and 8 per cent ash; all the ash was assumed to be SiO_2. - 14 + 28 mesh coke was used in the first three charges, - 20 + 100 mesh coke in several of the following ones, and unsized - 6 mesh material was used in the final charges. The different sizes of the coke seemed to make very little difference in the smelting operation. But when a fine powdered carbon was used, it was forced out of the crucible by the CO gas given off in a geyser-like spray, and it settled as a fine powder all over the room. This powdered carbon was used only on a preliminary run made by Professor Spielman.

The lime used was pure powdered CaO.

The CaF_2 added was also a powder.

Quantitative Methods of Analysis

Chromium:

0.3 gram of - 100 mesh concentrates was fused slowly in a porcelain crucible with about 5 grams of sodium peroxide until the material became a homogeneous greenish-black liquid. This was cooled, submerged in water, and

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allowed to digest completely. Then the liquid was boiled to break down excess peroxide and remove the oxygen, filtered, and washed thoroughly. The residue was saved for the iron determination. The filtrate was acidified with 1:1 H_2SO_4 to about 25 cc. excess, diluted to about 800 cc. with cold water, and titrated. A measured excess of standard ferrous ammonium sulfate was added first, then the solution was titrated back to a delicate pink with 0.1 N. $KMnO_4$ solution. The ferrous ammonium sulfate was standardized against the $KMnO_4$ solution each time it was used.

Iron:

The residue from the chromium filtration was washed into a beaker and dissolved in a warm mixture of HCl and water (about 10 cc. HCl and 15 cc. water). 20 mesh zinc was added and the solution warmed gently to reduce the Fe^{+++} to Fe^{++}. After the solution turned clear, about 50 cc. of cold water followed by 10 cc. of concentrated H_2SO_4 were added. The solution was then poured through a cotton filter, diluted to 800 cc. with cold water, and titrated to a delicate pink with 0.1 N. $KMnO_4$ solution.

Work with Graphite Crucibles

Several preliminary smelts were made in a standard graphite crucible in order to see how well the crucible would stand up. The first charge consisted of 200 grams of chromite concentrates, enough silica to make a sub-silicate slag, and 30 per cent excess coke over that

theoretically required to reduce all the iron and chromium.
The furnace was heated almost to white heat, then turned
off, and the thoroughly mixed charge was poured in. In
about ten minutes CO gas started to come off and continued
to come off until near the end of the melt. The charge
was slowly melted down, forming a very viscous slag above
the metal. The "motor effect" of the furnace was very
noticeable as it kept the melt well stirred up. The
crucible was covered during most of the melt in order to
hold in the heat and to keep the graphite crucible from
being subjected to the air. After about 30 minutes, the
smelted charge was poured into a graphite lined mold. The
walls of the crucible were partly eaten away at the slag
line, probably indicating that the slag contained metallic
oxides at this point and therefore that more excess carbon
should be used.

The next charge contained 40 per cent excess coke and
enough silica to make a singulosilicate slag. The smelt
was made as before in the crucible. Examination of the
crucible after pouring out the charge showed that the walls
were corroded somewhat more but not so badly that the
crucible could not be used again.

The third charge contained 50 per cent excess coke and
a little more silica than the previous one. Toward the
end of the melt a small hole appeared in the side of the
crucible, at which time the charge was poured out.

The corrosion of the crucible seemed to be due to both

chemical and mechanical action. Theoretically the
graphite walls should have been only slightly attacked
since there was a large excess of carbon in the charge.
The walls of the crucible were rather rough so that the
action of the melt as it boiled around due to the motor
effect could have mechanically torn the graphite particles
away, especially if aided by some oxidation of the carbon
to CO. Graphite is very soft, having a hardness between
1 and 2 as shown in Table 6 .

Most of the smelts for determining suitable slags,
which are described in the following section, were conduct-
ed in graphite crucibles turned out on a lathe from a
threaded graphite electrode pin. Each melt corroded the
crucible sides a little deeper, but since the walls of the
crucibles were thicker than those of the standard graphite
crucibles, more charges could be smelted in each one. After
about eight charges had been smelted in the first one, it
was patched with norblack, a specially prepared lampblack
put out by the Ajax Northrup Company. This norblack was
mixed with water into a paste and molded around the inside
of the corroded graphite crucible and dried slowly. This
resulted in a very smooth lining with few cracks.

Since the above eight charges contained a large amount
of graphite torn from the crucible sides, the slags could
not be examined with any degree of accuracy. Therefore this
graphite was separated by hand from each solid charge, and
the resulting graphite-free charges were remelted separately

and examined closely. In putting these charges in the furnace for remelting, the metal was placed on the bottom and the slag piled in above it. Seven of these melts were carried out successfully with practically no corrosion of the crucible. The eighth one was charged to the furnace with the slag on the bottom and the metal on top. This time the metal melted, but the slag just slightly fused and stuck to the bottom. The cause of this is fairly evident. The norblack patching, which is a much poorer conductor of electricity than graphite, was considerably thicker on the bottom than on the sides, therefore the bottom would naturally be cooler than the sides. Then as long as the metal was placed on the bottom it would readily melt, since the metal itself is a very good electrical conductor, and hold the slag away from the bottom as well as heat it up. But when the non-conducting slag was placed on the bottom it would not get hot enough to melt.

The remaining charges described in the following section were smelted in another crucible of this same type. This time the crucible was patched with norblack after each melt just as soon as the furnace had cooled sufficiently. The first smelted charge was separated from the loose graphite and remelted in the patched crucible for examination. But the rest of the charges could be examined directly without any remelting, since not as much graphite was torn loose each time. This method was fairly successful, but the time for smelting was increased since the norblack patching is

not as good a conductor as graphite.

Slags

A good slag should have a low formation temperature, a low melting point, and a low specific gravity. It should also be free running within 100 or 200 degrees centigrade of its melting point, and it should be reasonable cheap.

Slags are commonly classified for metallurgical purposes according to their silicate degree, which is the ratio of the weight of oxygen in the acid to the weight of oxygen in the base. If this ratio is less than one the slag is termed sub-silicate; if equal to one, singulosilicate; if one and one-half, sesquisilicate; if two, bisilicate; and if three, trisilicate.

The most common bases are CaO, MgO, BaO, FeO, and MnO, while the most common acid is SiO_2. Al_2O_3 may react either as an acid or a base and its reaction is practically unpredictable, but in making calculations it is usually considered a base.

Table 1, from Hofman and Hayward[11] was used by the author as a basis for calculating silica and lime additions.

Production of a good slag with all the above-mentioned properties from chromite concentrates is difficult because of the high Al_2O_3 and MgO content, since the action of the Al_2O_3 is unpredictable and the MgO in such large excess makes a slag with a very high melting point.

The most logical fluxes to add are: silica to lower the

1 lb. base requires pounds SiO_2 to form a			Name of Base
Singulosilicate	Sesquisilicate	Bisilicate	
0.535	0.803	1.070	CaO
0.196	0.294	0.392	BaO
0.750	1.125	1.500	MgO
0.873	1.310	1.747	Al_2O_3
0.416	0.625	0.883	FeO
0.422	0.633	0.845	MnO

1 lb. SiO_2 requires pounds base to form a			Name of Base
Singulosilicate	Sesquisilicate	Bisilicate	
1.86	1.24	0.93	CaO
5.10	3.40	2.55	BaO
1.33	0.88	0.66	MgO
1.14	0.76	0.57	Al_2O_3
2.40	1.60	1.20	FeO
2.36	1.57	1.18	MnO

Table 1 - Silica and base equivalents for various types of slags.

melting point, fluorspar (CaF_2) to make the slag fluid, and lime to decrease the high per centage of MgO and form compounds with lower melting points. Melting points of various slag constituents are shown below in Table 2.

$2\ MgO.SiO_2$	$1890^{\circ}C$	$5\ CaO.2Al_2O_3$	1455 ± 5
$MgO.Al_2O_3$	2135 ± 20	$CaO.Al_2O_3.2SiO_2$	1550 ± 2
$CaO.SiO_2$	1540 ± 20	$2CaO.Al_2O_3.SiO_2$	1590
$CaO.Al_2O_3$	1600 ± 5	$CaO.MgO.2SiO_2$	1391
$3\ CaO.5Al_2O_3$	1720 ± 10	$2CaO.MgO.2SiO_2$	1458

Table 2 Melting Points of Slag Constituents[10]

The melting point of pure ferrochromium containing fifty per cent Cr and 34 per cent Fe as obtained from the Cr-Fe constitutional diagram[3] is approximately 1550 degrees Centigrade. Since the addition of carbon to the metal lowers the melting point, this figure can be considered as a maximum temperature.

Calculation of a satisfactory slag for the ore which will have a low melting point and a low free-running temperature is almost impossible since there are five constituents present and since the reaction of the Al_2O_3 is unpredictable. Therefore a moreorless cut-and-try method was used. Table 4 shows the charges smelted.

The first charge contained only chromite concentrates plus coke in excess. The next three charges (2,3,4) consisted of chromite, excess coke, and silica varying in amounts to yield in succession a subsilicate, a singulo-

Concentrates = 200 grams

Cr_2O_3 – 43.8% = 87.6 g. ----------- O = 27.6 g.

FeO – 27.0% = 54.0 g. ----------- O = 12.0 g.

MgO – 15.0% = 30.0 g.   39.6 g. O to be

Al_2O_3 – 17.0% = 34.0 g.   reduced with carbon.

CaO – 1.6% = 3.2 g. $C + O \longrightarrow CO$

SiO_2 – 3.4% = 6.8 g.   C required$(39.6 \times \frac{12}{16})$=29.7g.

Coke is 92% C.

For a singulosilicate slag   Coke req'd = $\frac{29.7}{.92}$ = 32.1g.

                    SiO_2 needed   30% excess(.3x32.1)= 9.6g.

For MgO: 30.0x.75 =   22.5 g.   Total coke to add = 41.7g.

For Al_2O_3: 34.0x.873 = 29.7 g. SiO_2 in this coke:

For CaO: 3.2x.535 =   1.7 g.   41.7 x .08 = 3.3 g.
                    53.9 g.

For a subsilicate slag (2/3 x singulo)

        53.9 x 2/3 ---------------- 35.9 g.

        Less SiO_2 in chromite ----- 6.8 g.
                                29.1 g.

        Less SiO_2 in coke ---------- 3.3 g.

        SiO_2 to add to charge ----- 25.8 g.

Charge:

        Chromite conc. ------ 200 g.

        Coke ---------------- 41.7 g.

        Silica -------------- 25.8 g.

                Total ------- 267.5 g.

Table 3 Charge Calculation

Charge No.	Chromite	Coke	Silica	CrF$_2$	CaO
1	160	40.0	----	--	--
2	200	41.7	26.0	--	--
3	120	27.2	26.0	--	--
4	120	29.3	42.0	--	--
10	60	16	12.5	--	--
11	60	16	12.5	1.0	--
12	60	16	12.5	1.5	--
13	60	16	12.5	2.0	--
14	60	16	14.5	1.1	3.0
15	60	16	16.0	1.1	6.0
16	60	16	17.5	1.1	9.0
17	60	16	19.0	1.1	12.0
18	60	16	15.0	1.1	5.0

Table - 4 Charges Smelted for Determination of Best Slag

Charge No.		Wt.	% Cr	% Fe	Cr:Fe
	Metal	28.5	50.4	33.5	1.50
11	Slag	16.2	0.9	1.8	0.5
12	Metal	25.1	51.6	35.0	1.47
	Slag	18.8	1.4	1.0	1.4
13	Metal	26.8	53.4	31.9	1.67
	Slag	25.0	----	----	----
14	Metal	27.9	48.9	34.7	1.40
	Slag	30.4	----	----	----

Table - 5 Weights and Analyses of Several Metals and Slags

silicate, and a sesquisilicate slag. Al_2O_3 was calculated as a base as shown in the sample calculation given in Table 3.

In the next four charges (10, 11, 12, and 13) the silica and coke were kept constant while the CaF_2 was varied from 0.5 grams to 2.0 grams. The following four charges (14, 15, 16, and 17) contained lime varying from 3 grams to 12 grams, CaF_2 and coke constant, and silica to make singulosilicate slags. The final charge was run as a check.

Slag No. 1 was very viscous with a very high melting point.

Slag No.'s 2,3, and 4 were all very viscous, but not as bad as No. 1. No. 2 appeared to be worse than No.'s 3 and 4, and since the amount of fluxes should be reasonably small, a singulosilicate slag, No. 3, was chosen as best.

No. 10 was somewhat sticky and not very fluid, with a high melting point.

No. 11 was fairly fluid, easy to pour, not as sticky as No. 10, but with a high melting point.

Slag No. 12 was a little more viscous than No. 11.

Slag No. 13 was very sticky and hard to pour.

No. 14 was somewhat sticky, more fluid than No. 11, with a fairly low melting point.

No. 15 was not sticky, had a low melting point, low formation temperature, and was fluid enough at the operating temperatures.

No. 16 was similar to No. 14 but no better.

No. 17 had a low melting point but seemed to be rather viscous. There was a large quantity of slag here.

The above-mentioned melting-point comparisons were based upon the author's judgment and not upon pyrometer measurements. From the above observations, it was concluded that a slag approximating 14 or 15 was best. No. 18 was run as a check, and the slag formed confirmed this first conclusion.

All the products were weighed and as many of them were assayed for chromium and iron as time permitted. Since all the charges contained excess carbon and were held in the crucibles until reduction was complete, the amount of metal obtained each time was about the same, as shown in Table 5 . Because of the small amount of concentrates smelted per charge, the per centages of metal and slag losses were high.

Work with Crucibles Other than Graphite

Obviously, if the charge were in contact with white hot graphite throughout the smelting operation, practically all the iron and chromium would be reduced. Since the author wished to carry out experiments on selective reduction of the iron, a refractory crucible other than graphite was desired. Table 6 gives a list of the most common refractory materials with their melting points and hardness.

The graphite was first replaced with a standard alundum crucible. A charge of pure chromite was placed in the crucible and the power was turned on for almost an hour.

Compound	M. P.	Hardness	Compound	M.P.	Hardness
Al_2O_3	2050° C.	9	MgO	2800° C.	5
BeO	2400° C.	9	$MgO \cdot Al_2O_3$	2135° C.	8
SiC	2300° C.	9.5	ThO_2	3000° C.	–
Cr_2O_3	2275° C.*	–	Yt_2O_3	2410° C.	–
C	over 3000° C.	1-2	ZrO_2	2720° C.	–
CaO	2570° C.	3-4	Chromite	2180° C.	5.5

* 1990±20 according to International Critical Tables

Table 6 Melting Points and Hardness of Refractories

During this time the charge didn't even get warm, showing
definitely that the chromite is not a conductor. Therefore
some scheme was necessary whereby a refractory lining could
be placed inside a conducting graphite crucible.

Since there was about 7/16 inch of clearance between
the outside of the standard alundum crucible and the copper
coils (See Figure 5), a 1/4 inch packing of a conductor
such as powdered graphite around the alundum crucible and
a 3/16 inch ring of insulation around the conductor seemed
feasible. A sheet of asbestos was substituted for the nor-
sil packing around the sides and the regular norsil powder
was placed on the bottom as usual except that this layer
was put in only one-half as thick to allow some room for
conductor to be packed on the bottom as shown in Figure 6.

At first, powdered amorphous carbon was packed in
around the alundum crucible, but the crucible got just
slightly warm after the power had been turned on for over
an hour. Next, an old graphite plate, previously used as

Normalith
Alundum
Norsil
Mica

Plan   Section AA

Scale: 1" = 2"
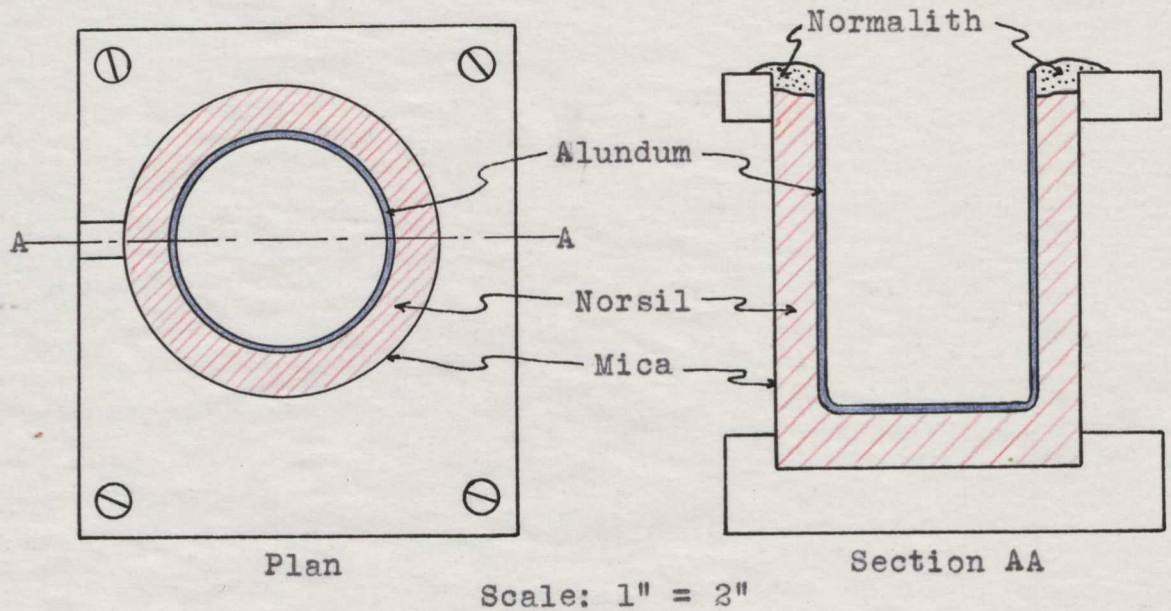
Figure 5 – Furnace with Standard Alundum Crucible.
Coils are not shown.

Normalith
Asbestos
Alundum
A
Graphite
Norsil
Mica
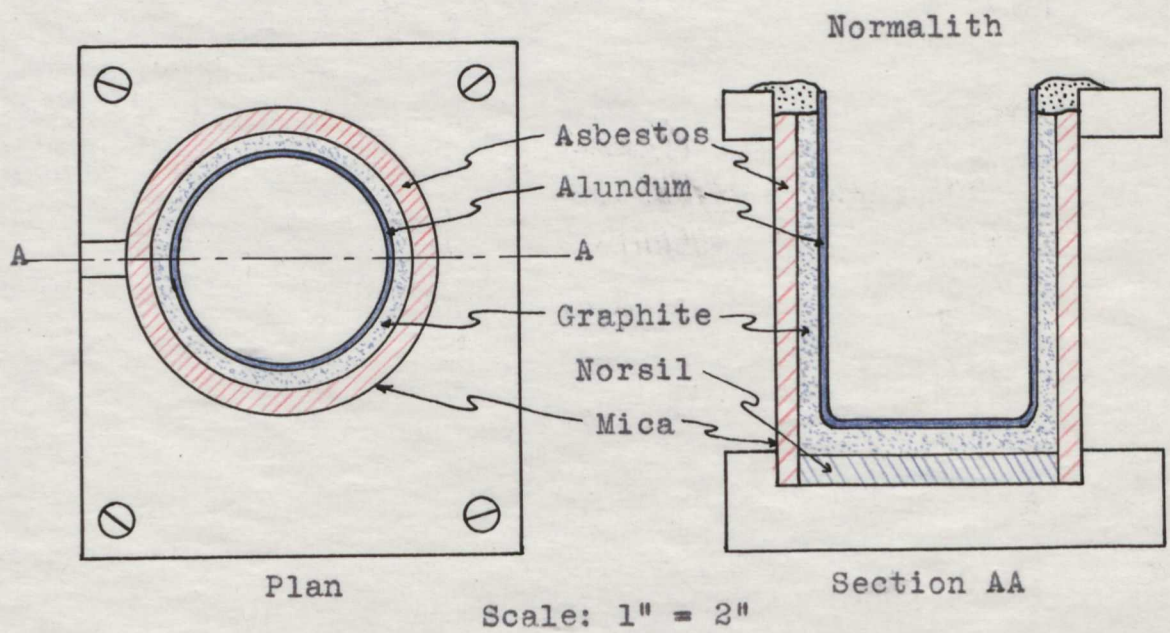
Plan   Section AA

Scale: 1" = 2"

Figure 6 – Furnace with Standard Alundum Crucible
Surrounded by Crushed Graphite. Coils
are not shown.

an electrode in a resistance furnace, was ground to -6 mesh
and packed around the alundum crucible. This time the fur-
nace got up to bright red heat, estimated at 1050° C. to
1150° C. but still this was not hot enough since temperatures
of about 1700° C. to 1800° C. were necessary. Incidently,
due to the smaller amount of insulation used, the cooling
water from the coils got several degrees hotter, but not
above safe operating temperatures.

This same graphite packing was tried a second time
using the same crucible. This time every effort was made
to tamp the graphite down as hard and tight as possible.
Again the furnace got to bright red heat but not to white
heat.

An inch was cut off the top of the alundum crucible
in order to make room for better insulation and more graphite
underneath the crucible, (see Figure 7) but still the tem-
perature attained was too low.

Some alundum thimbles 1 3/4 inches in diameter and
3 7/8 inches high, which were made for collecting flue dust,
were obtained. One of these was substituted for the alundum
crucible. This allowed about ½ inch for graphite packing
and 3/8 inch for the usual insulation. Asbestos insulation
was used again, and the graphite was packed inas shown in
Figure 8. This time the crucible got hotter than those of
the previous attempts, but not quite hot enough. In the next
attempt the thimble was placed inside a standard alundum
crucible and the graphite packed still harder, but the re-
sults were still negative.

Plan   Section AA

Scale: 1" = 2"
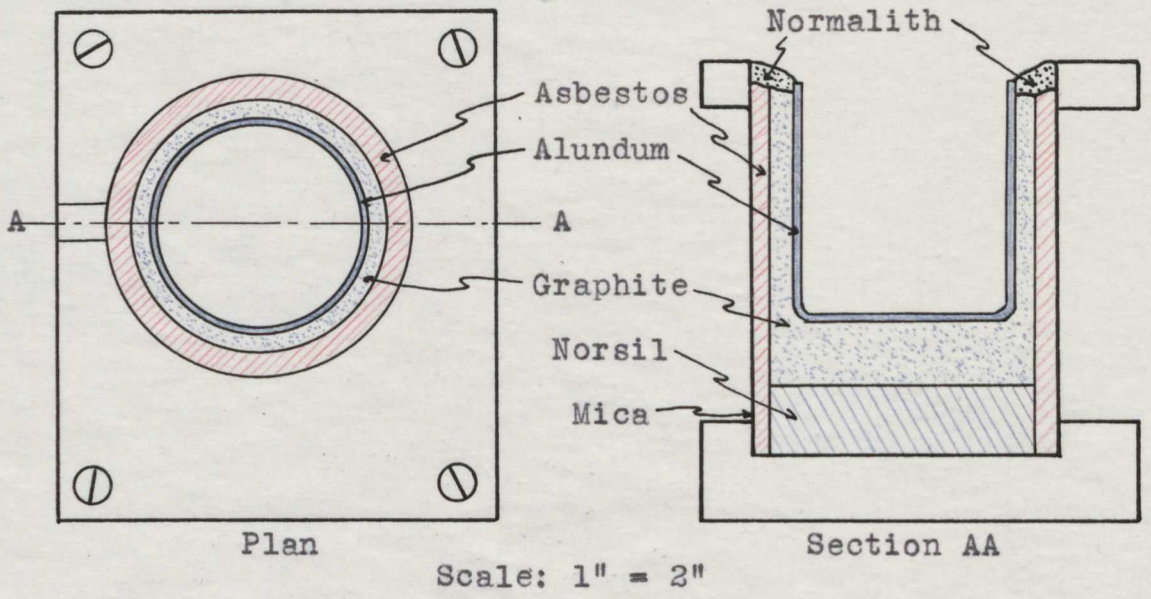
Figure 7 – Furnace with Standard Alundum Crucible
Shortened by One Inch. Coils are not
shown.

Plan   Section AA
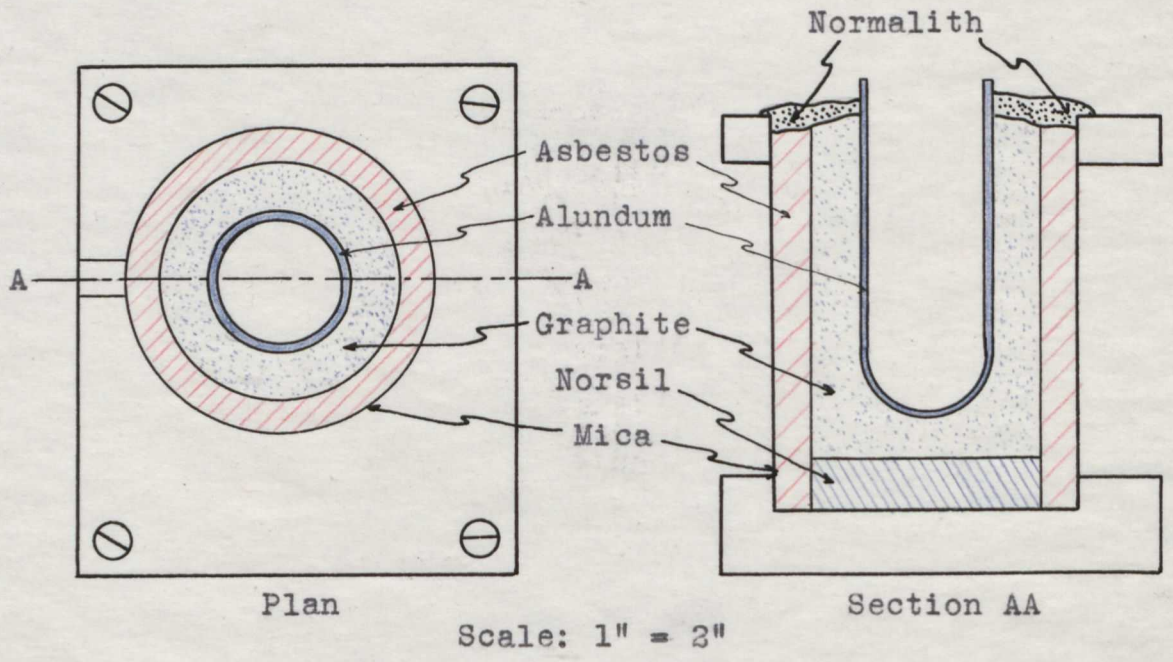
Scale: 1" = 2"

Figure 8 – Furnace with Alundum Thimble Surrounded
by Crushed Graphite. Coils are not shown.

The above experiments with graphite packing seemed to indicate that the amount of graphite used was not as important as the closeness with which it was packed. This led to the idea of making a packing similar to a commercial solderberg electrode, which consists of graphite or carbon bound together with pitch or tar and baked.

Some tar used for patching roofs was heated in front of a muffle furnace and mixed in small batches with -6 mesh graphite containing considerable fines. The mixing dish and coke were kept very hot, and just enough tar was added to make the graphite stick together. Each batch was thoroughly mixed and packed very hard around an alundum thimble 1 3/8 inches in diameter which was set inside a tin can 2 5/16 inches in diameter.

This can containing the crucible was placed upon a hot plate and kept at about 80 degrees Centigrade for 24 hours, during which time fumes from the tar came off. The following afternoon the crucible, still surrounded by the can, was kept in front of a muffle furnace for about six hours, the can being turned frequently to keep the heat fairly well distributed. All during this time dirty black fumes were given off, but the crucible was not brought up to red heat. The following day the crucible was placed inside the muffle and the temperature was raised to red heat. The can was then removed from the outside and the muffle was closed and held at this temperature for several minutes. After this, the crucible was removed, cooled,

and fitted into the electric furnace. The power was turned on for over an hour, but the crucible did not even get red hot, although it did get very warm. Since this crucible had been baked only a few minutes, the author decided to seal it in the Hoskins Electric Furnace mentioned before and bake it for a longer time at higher temperatures in a reducing atmosphere. But at this time another crucible scheme with much more promising prospects was hit upon.

A threaded graphite electrode pin was put on a lathe and made into a graphite sleeve with the following dimensions: inside diameter, 1 5/16 inches; outside diameter, 2 1/4 inches; inside height, 3 inches; and outside height, 3 1/2 inches. An alundum thimble like the one used previously was slid down into this sleeve. When this was placed in the furnace and the power was turned on, it became white hot inside of 15 minutes. This crucible and sleeve combination looked like Figure 8, with the broken graphite replaced with a solid ring of graphite securely bound together.

A charge consisting of chromite concentrates, coke in excess, and enough silica to make a singulosilicate slag was placed in the alundum thimble within the graphite sleeve. After smelting and pouring out the melt, it was discovered that the alundum thimble had been entirely eaten away. The temperature seemed to be higher than that obtained when the standard graphite crucible was used. It was thought that the silica added may have caused a reaction

with the crucible.

Therefore, another alundum thimble was placed in the sleeve and a charge consisting of chromite concentrates, coke in excess, and lime was smelted this time. Again the whole crucible disappeared into the melt. The author finally concluded that either the temperatures attained were above the melting point of Al_2O_3 or the chromite itself reacted with the Al_2O_3 at this very high temperature. Since gases were always evolving from the melt and from the graphite sleeve, no accurate pyrometer measurements of the temperature could be taken. The Ajax-Northrup Company claims that the furnace temperatures may be obtained as high as 2500° C. with their crucibles, and it is the author's opinion that temperatures almost as high as this were obtained during the two preceeding smelts. The crucible got white hot faster than, and the graphite sleeve used was at least $1\frac{1}{2}$ times as thick as, the standard graphite crucible put out by the company. The melting point of Al_2O_3 is 2050° C. as shown in Table 6. These two failures with Al_2O_3 crucibles led the author to conclude that some refractory other than Al_2O_3 should be used for chromite smelting.

Powdered MgO was mixed into a paste with water glass and molded around the inside of a standard graphite crucible. This was dried two days in the laboratory at room temperature, during which time small cracks began to appear throughout the lining. Then upon slowly heating in a muffle furnace, the cracks became larger and small pieces began to

spall off. Finally, when put into the induction furnace and heated to red heat, the whole MgO lining began to disintegrate and it was discarded.

A machined graphite sleeve was lined with a paste of powdered MgO and water. This lining was allowed to dry overnight during which time several cracks began to develope in it. Upon heating slowly in the electric furnace, the lining developed a great number of small cracks, and soon it began to disintegrate and spall off. Evidently the powdered MgO was too fine and a coarser material should have been mixed with it.

A magnesite (MgO) brick was crushed, ground to pass -14 mesh, and screened on a Ro-Tap into the following sizes, -14 +20, -20+28, -28+48, -48+100, -100+200, and -200. This screened material was roughly measured out in the following proportion:

```
2 parts  -  28+48
2 parts  - 48+100
4 parts  - 100+200
10 parts  - 200
```

This was placed upon a glass plate and kneaded with water into a fairly plastic mass until it was thoroughly mixed together, then it was carefully molded around the inside of a standard graphite crucible. It was dried at room temperature for 24 hours and on a hot plate for about 3 hours. Then it was placed in the furnace and very slowly brought up to red and then white heat. The crucible became very firm and solid except in two small patches where it had been injured slightly; here it crumbled and caved in,

leaving two small holes. A charge was placed in the crucible and smelted. The ferrochromium reduced easily, but in an attempt to get a good slag, some silica was thrown in on top of the sintered material. This silica immediately began to attack the crucible and dissolve it into the melt.

Another MgO crucible was made using the same proportions of screen sizes, except that this time about 2 parts of powdered MgO were mixed with it. The crucible was dried at room temperature for 22 hours and on the hot plate for 5 hours. Again it was placed in the induction furnace, slowly heated up to a white heat and held at this temperature for an hour. Then it was slowly cooled and examined. A very hard, firm crucible with no cracks at all had been formed. The following charge was placed in it and smelted:

$$Chromite - 80 \; grams$$
$$Coke \quad\;\; - 20 \; grams$$
$$Silica \quad\; - 12 \; grams$$
$$CaF_2 \quad\;\; - 1.4 \; grams$$
$$CaO \quad\;\; - 6 \; grams$$

The ferrochromium was easily reduced and poured off, but the slag remained very sticky and clung tenaciously to the sides of the crucible, attacking it and eating it away. The resulting metal weighed 39.6 grams, showing that it had all been reduced from the charge. Lack of time prevented further investigations, but the author concluded that MgO is a suitable refractory to be used in this furnace and that future work upon basic slags in this type of crucible is justified.

CONCLUSIONS

Unsized, - 6 mesh coke is a good reducer to use in smelting chromite to ferrochromium in the Ajax Northrup induction furnace.

Graphite crucibles are satisfactory for chromite smelting if they are patched after each charge is poured. Norblack patching is satisfactory but smelting time is increased because the norblack is not as good a conductor as graphite. Corrosion of graphite crucibles is due to both chemical and mechanical action.

A singulosilicate slag with proper additions of fluorspar and lime has a fairly low melting point and is free running at operating temperatures. Too much or too little fluorspar produces a poor, sticky slag. Small additions of lime are helpful.

Alundum is definitely not the kind of refractory to be used with chromite.

A graphite packing around a refractory crucible must be very solidly bound together. None of them made by the author with ordinary means were successful.

Powdered MgO alone is too fine to be used in making a refractory crucible. Sodium silicate is not a good binder to use here, water being more suitable.

MgO mixed in the proper proportions of sizes and bound together with water makes a hard, firm crucible with no cracks if dried and baked in the correct manner. Although no successful smelts were conducted in this type of crucible, it has good possibilities if the slag is basic enough.

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