

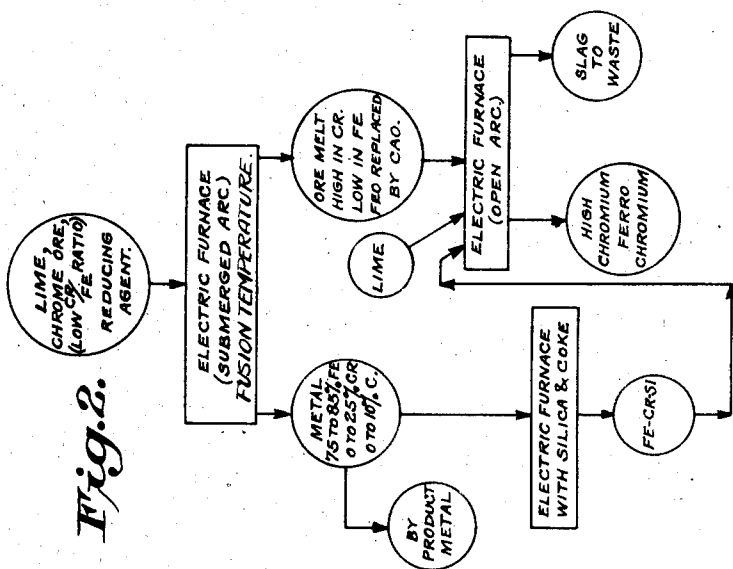
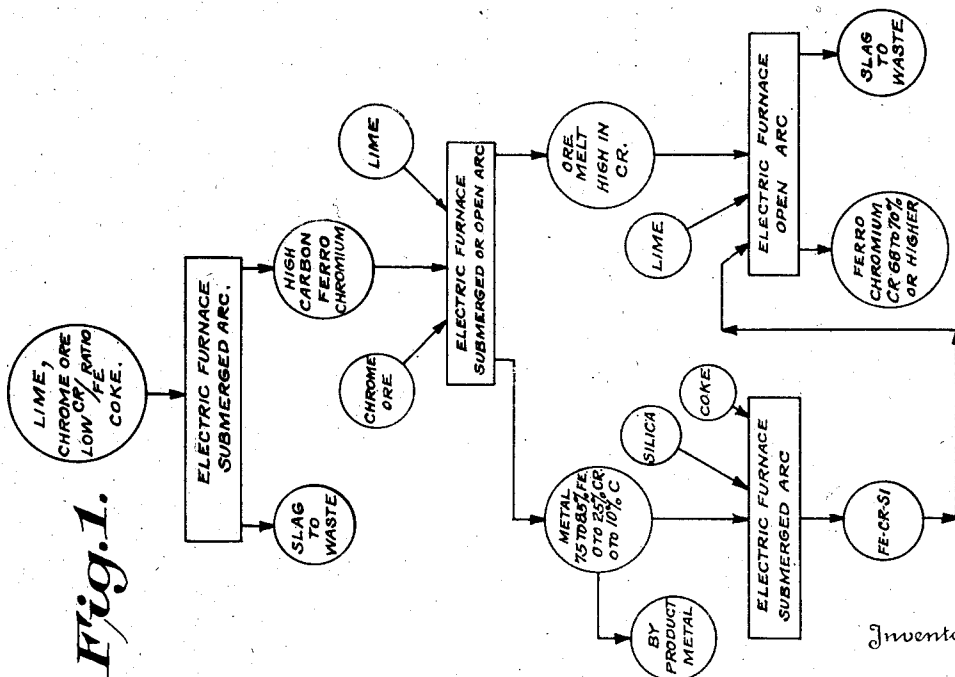
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MANUFACTURE OF CHROME ORE PREPARATIONS

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MANUFACTURE OF CHROME ORE
PREPARATIONS

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22 Claims. (Cl. 75-1)

This invention relates to manufacture of chrome ore preparations; and it comprises an ore preparation containing a substantial amount of lime chromite and representing a chrome-iron ore with some, or all, of its combined iron content subtracted and replaced by calcium, the ore preparation being chemically basic, glassy in its solid state and having easy smelting characteristics; and it further comprises a process wherein the ore is fused with an addition of lime in the presence of enough carbon to reduce iron, thereby producing a layer of molten iron of low chromium content and a melt of high chromium content, the iron and the melt being collected and withdrawn separately; all as more fully herein-after set forth and as claimed.

Chromite or chrome iron ore is at present substantially the only commercial source of chromium and chromium compounds. In a pure state, chromite is $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and contains about 46 per cent Cr and 25 per cent Fe; a chromium:iron ratio of about 64.8:35.2.

In many natural ores, however, the FeO of the ideal chromite is partially replaced by other oxides such as magnesia, and the Cr_2O_3 is often replaced by alumina, the chromium:iron ratio being higher or lower, respectively, because of such replacement. A typical replacement of the first-mentioned type, increasing the chromium:iron ratio, is found in New Caledonia chrome ores which are at present imported into the United States for making chromium alloys. A typical analysis of a New Caledonia chrome ore shows 45.71 per cent Cr_2O_3 and 11.67 per cent FeO ; a chromium-iron ratio of 77.5:22.5. This ratio appears to be a maximum for commercial ores. Such an ore, upon reduction in the electric furnace by customary methods gives a ferrochrome of about 70 per cent chromium content as a maximum. Ferro-chromes of higher than 70 per cent chromium content are desirable commercially. For these higher chromium contents it has been necessary to use chromium oxid made from bichromates produced from chrome ore.

One of the principal uses of chrome ore is in the production of ferrochromium and for this it is desirable to have the chromium-iron ratio in the ore as high as possible so as to permit a high chromium content in the product. At present in all cases the richness in chromium of a ferrochrome is limited by the Cr:Fe ratio of the ore used.

In some natural ores, the Cr to Fe ratio is the same as that exemplified in the New Caledonia ores but the content of chromium much less. In

others the iron content is increased to such an extent that the chromium ratio is well below that of ideal chromite. An abundant supply exists of domestic ores and Canadian ores of this type, a typical analysis showing 40.89 per cent Cr_2O_3 and 21.05 per cent FeO or a Cr:Fe ratio of 63 to 37. Such ores have been considered low grade or off grade and are not used for production of high chromium ferrochrome.

In the present invention I make it possible to use these low grade chrome iron ores in high grade ferro-chromium production by first producing in the electric furnace a basic chromite ore of subtracted iron content and, when desired, of added chromium content. The artificial basic chromite ores can then be used as a raw material, so to speak, in processes for the production of iron-chromium alloys. I have found that these natural chrome ores can be beneficiated for ferrochrome production by selectively reducing and removing iron from the ores, leaving altered ores of heightened chromium oxid content with iron in any desired ratio lower than that of the raw ore. If desired, the iron in a natural chrome ore can be substantially completely removed, producing an ore product from which there can be obtained, by reduction with silicon, practically pure chromium metal.

Low carbon ferrochromium of any desired chromium content can be produced by reducing the beneficiated ore with relatively low grade ferrosilicon; complete control of the chromium content being attained by coordinating with the extent of iron subtraction from the ore the grade or silicon content of the ferrosilicon used for reducing the beneficiated ore.

While in other ways of operating, I use carbon as the reducing agent, in one embodiment of my invention, a portion of natural chrome ore is reduced in an electric furnace with a suitable reducing agent to produce total reduction and a ferrochromium of a composition corresponding to the chromium-iron ratio of the ore; this ferrochromium being then utilized as a reducing agent. The natural ore to be treated is smelted with this ferrochromium under conditions providing a basic melt. The chromium of the ferrochromium reduces iron from the second ore portion with oxidation of the chromium; the reduced iron leaving the system as a byproduct. The oxidized chromium joins the ore to form a basic ore melt of heightened chromium content, and lowered iron content; this melt constituting the new basic ore. The reduced iron and the melt are separately tapped off and leave the system. Thus chromium

from the first portion of ore is transferred to the second portion to produce a concentrated basic chromite ore product which may be substantially free of iron and from which ferrochrome of any desired grade or chromium metal can be readily produced by reduction with ferrosilicon or with silicon as reducing agent. The iron left after the operation contains a substantial percentage of chromium and constitutes a valuable byproduct. A portion of it can be used in making ferrosilicon or ferrochrome silicon for reduction of the concentrated chromium ore to produce high chromium ferrochrome; the chromium contained in the iron byproduct so used being added to the ferrochrome. The low chromium iron metal byproduct, being usually low in carbon, is readily and economically converted into low carbon chromium steel by known methods.

In the embodiment of my invention as just described, the chromium of ferrochromium serves as reducing agent in removing iron from natural chrome iron ore. This has the advantage of adding to the chromium content of the ore as well as subtracting from the iron content. However, other reducing agents can be used. Carbon as coke or charcoal, silicon, silicon alloys or silicides and aluminum may be used, the proportions being such as to selectively reduce iron from the ore and to leave the chromium oxid for the most part unreduced.

In the preparation of the low iron chrome ore of the present invention the natural ore is fluxed by an addition of lime; in effect replacing FeO in the ore with CaO and forming calcium chromite, $\text{CaO} \cdot \text{Cr}_2\text{O}_3$. This replacement has the effect of concentrating the chromium content of the ore to give a product of higher chromium content than the original natural ore. It also makes the product more fusible and easy to smelt for reduction of chromium to metal. In this reduction the silica, alumina, magnesia, etc. of the ore is slagged off in a basic slag and it is advantageous to put the required base into the ore when the iron is being reduced and removed. The altered chrome ore of low iron content is then ready for reduction. Reduction of the contained chromium may be effected without allowing the fluxed ore melt to solidify. Preparation of the melt and its reduction or smelting may be carried on in a single furnace. Usually in preparing the ore melt, lime, CaO, is added in a proportion of about 1.75 or 2 parts by weight for each part of silica contained in the ore. When added in this proportion, sufficient lime is provided to react with chromium oxid in the ore with formation of a calcium chromite. In fact, when a natural chromite ore is fluxed with lime there is a replacement of FeO by CaO even in the absence of a reducing agent. When the iron oxid is also reduced as it is displaced the reaction between lime and chromium oxid may proceed to completion.

In the practice of my invention, considerable leeway is permissible in the amount of carbon or other reducing agent used in reducing iron from natural chrome ore. The amount used in proportion to the ore depends upon the grade of the chromium alloy to be produced from the concentrated chrome ore product. It is usually advantageous to use sufficient reducing agent to reduce to metal all of the iron in the ore and a small part, say 3 to 10 per cent, of the chromium. This gives an ore melt substantially free of iron and containing upwards of 90 per cent of the chromium in the original ore. The reduced iron con-

taining a substantial percentage of chromium is useful in making chrome steels. When silicon is used as reducing agent sufficient chromium may be put into the iron to make stainless steel or stainless iron.

The non-metallic portion of the melt is liquid at the temperature of the furnace. On cooling it sets to a vitreous or glassy solid; the new material of the present invention. It has practically the chromic oxid content of the original ore, without substantial diminishment, but the original FeO has been replaced to a greater or less extent by CaO. The new material is basic in nature, and as stated is readily fusible.

All or most of the FeO can be subtracted, giving an ore adapted for making chromium and its non-ferrous alloys. But generally I make an altered ore still containing some iron and adapted for making high grade ferrochrome. Altered ores containing some iron are easier to make, fuse and use than the straight calcium chromite.

The ore products described are most advantageous materials for making carbon-free ferrochromium of any desired content, or pure chromium metal. The material can be further processed directly, while it is still in its molten state, or it can be taken from the furnace, cooled and shipped to the ferrochrome manufacturer, to serve as a raw material in ferrochrome alloy manufacturing. It is of a composition and physical condition very suitable for steel making, being superior to natural chromite ores in this respect. Thus from a low grade chromium-poor, high iron natural ore there is produced a high chromium artificial ore which is equal to or superior to high grade natural ores.

When the ore is prepared free of iron, it is possible to use ferrosilicon of any grade for reducing the chromium oxid of the ore; the chromium content of the ferrochrome produced being a matter solely of the grade of ferrosilicon used in reduction of the ore. Reduction of the chromium oxid being a function of the silicon in the ferrosilicon aided by the base replacing iron oxid in the original natural ore, it is a simple matter to control the chromium content of the ferrochrome produced by having a proper silicon content in the ferrosilicon used for the reduction. For example, a substantially carbon free ferrochromium with over 70 per cent chromium can be produced by reduction of the prepared iron-free basic ore with 50 per cent ferrosilicon. When it is desired to make a low chromium ferrochrome, say of 30 per cent chromium content, a 15 per cent ferrosilicon serves for reducing agent. An 88 per cent ferrochromium is made from 75 per cent ferrosilicon. If 99 per cent chromium metal is wanted, it can be made by silicon of 98 per cent grade. Using ferrochrome silicon containing 20 per cent Si and 20 per cent Cr a metal containing 69 per cent chromium is formed. These reductions are advantageously effected in an electric furnace of the Heroult type. The low fusing point of the lime-fluxed ore of high Cr_2O_3 content makes for smooth, efficient furnace operation. However, the reductions can readily be effected by known exothermic processes using excess of silicon to furnish heat for melting with sodium nitrate or potassium chlorate as accelerator. In this operation the high lime content of the ore and its ready fusibility keeps slag losses of chromium at a minimum. Low carbon ferrochromium containing upwards of 70 per cent chromium can be produced directly by this exothermic process.

In manufacturing the altered chrome ore product of the present invention, electric furnaces of usual types are utilized. Two phase or three phase furnaces of the submerged arc type are suitable, also furnaces of the Heroult type utilizing unsubmerged arcs. The low chromium iron metal reduced from the ore separates as a molten layer beneath the high chromium ore melt, the two molten layers being tapped from the furnace and separated. When ferrochromium is to be made from the ore melt, it is possible to tap the iron alone from the furnace and to reduce the ore remaining in the same furnace but it is usually more advantageous in large scale operation, as I have found, to utilize a second furnace of the Heroult type for making ferrochrome or chromium metal in batches and to operate the first or iron-subtracting furnace continuously. It is usually of course economical to run the chrome ore concentrate while in molten form from the first furnace to a second or chromium reducing furnace. However, the chrome ore concentrate can be solidified and broken up for shipment to a distant reducing plant.

It is possible to make the described chrome ore concentrate by first producing high carbon ferrochromium from a natural chrome ore and by then oxidizing the chromium and carbon of this ferrochromium with ordinary iron ore (Fe_2O_3) in the presence of a lime-silica slag bath which may be formed by fluxing the usual silica of the iron ore with lime in a ratio of 1.75 to 2CaO to 1SiO_2 . So working, the chromium of the ferrochrome is oxidized and the iron oxid reduced under basic conditions, the products being a basic ore melt high in chromium and a metallic layer of a low carbon iron alloy low in chromium. The preparation of the altered chrome ore in this way can be regulated and adjusted by proportioning the ferro-chromium and iron one so as to produce a substantially iron-free chrome ore melt and an underlying metal of sufficiently high chromium content to allow of its use in making commercial chromium steel of various kinds. In fact the process can be so carried out as to give the proper chromium content in the reduced iron for any particular chromium steel; it being subsequently necessary only to add to the separated metal the customary deoxidizers and other desired constituents.

In a specific example of my invention, an altered chrome ore substantially free of iron and containing a substantial percentage of calcium chromite, the total chromium oxid content being 43 per cent Cr_2O_3 , is obtained from a Canadian chrome iron ore analyzing as follows:

	Per cent
Cr_2O_3 -----	40.89
Iron oxids calculated as FeO -----	21.05
Al_2O_3 -----	6.83
MgO -----	16.51
SiO_2 -----	9.94

The chromium-iron ratio of this ore being 63:37, it has heretofore had small value as a source of chromium alloys. It has heretofore been impossible to produce from such an ore a ferrochromium above 55 to 60 per cent chromium content, as can be done under the present invention.

In an example of the present invention applied to this ore 1000 pounds of ore is mixed with 164 pounds of burnt lime and 50 pounds of coke containing 80 per cent carbon. This ratio of carbon to ore is in slight excess over that merely necessary to metallize the iron content of the ore.

The ore and coke and lime are ground to pass through a $1\frac{1}{2}$ inch screen and are mixed and charged into an electric furnace of three phase submerged arc type. In submerged arc operation, sometimes called "arc resistance heating", the arc is formed by an electrode ending near the surface of the melt and passing through a body of unsmelted materials charged in for smelting; the electrode is surrounded by the incoming material. The operation of this type of furnace is continuous. In the furnace operation a temperature about 1600°C . is suitable and the charge is smelted in a continuous operation. From time to time a metal containing 3.8 per cent chromium, 0.54 per cent carbon and 95.66 per cent iron and a glassy ore melt containing 43 per cent Cr_2O_3 , 17.2 per cent CaO, and 10.4 per cent silica are tapped from the furnace and run into separate receptacles. From the charge given the yield of low chromium iron metal is 140 pounds and that of the altered ore is 953 pounds. Iron oxid present in the original ore as ferrous chromite is replaced by lime forming calcium chromite.

The concentrated ore, reduced in a Heroult furnace with 50 per cent ferrosilicon in a ratio of 953 pounds of ore to 220 pounds of ferrosilicon (50 per cent Si) yields 390 pounds of ferrochromium containing 71 per cent chromium and having a carbon content of 0.04 per cent.

In producing the new chrome ore material of the present invention from natural chrome iron ores, I have found that the reduced iron instead of being removed as such can be removed as a phosphid or sulfid by adding a phosphate or a sulfur compound to the furnace charge. For example, when phosphate rock is added to the furnace ore burden together with sufficient carbon to reduce the phosphorus of the rock, the iron metal reduced from the ore contains iron phosphid; ferrophosphorus of a desired grade being thus a byproduct of the beneficiated chrome ore, the lime of the phosphate rock replacing iron in the ore. When a high sulfur iron is desired, it can be produced simply by adding iron pyrites to the furnace ore burden.

While the invention as above described has particular utility in making available for chromium alloy production certain chrome iron ores hitherto considered off grade and not used, the new and altered chrome ore can be made with advantage from the high grade chrome ores, thereby making it possible to produce from these ores chromium metal and chromium alloys of higher chromium content than has hitherto been possible.

In the accompanying drawing I have shown diagrammatically flow sheets illustrating processes within my invention. In this showing,

Fig. 1 shows the steps of a process in which one portion of chrome iron ore is reduced to ferrochromium which may be made high in carbon, and this ferrochromium serves as reducing agent for a second portion of chrome iron ore which is beneficiated by removal of iron reduced by the chromium of the ferrochromium and by addition of chromium oxid formed in the reduction. The beneficiated chrome iron ore (ore melt high in Cr), the new product of the present invention, can be cooled and processed separately. In the process outlined in the flow sheet, however, the concentrated chrome ore melt is directly reduced by ferrosilicon, advantageously containing some chromium, with production of a ferrochromium containing more than 70 per cent chromium.

The ferro-chrome silicon reducing agent is advantageously made from the chromium-containing iron metal formed as a byproduct of the chrome ore concentration.

- 5 Fig. 2 shows a flow sheet of a process of making high grade ferrochromium from a chrome ore of low CR:Fe ratio which comprises the two steps: (1) raising the ratio of chromium to iron by replacement of iron oxid (FeO) in the ore with lime (CaO) accompanied by selective reduction and removal of the replaced iron and (2) thereafter reducing the altered ore with ferrochrome silicon; chromium-containing iron metal formed as a byproduct in step (1) being advantageously utilized in making the reducing agent for step (2).

10 Claims to a portion of the subject matter described and originally claimed in this application are being asserted in my copending application Serial No. 164,988, filed September 21, 1937, as a continuation-in-part of this application.

What I claim is:—

1. A manufactured chrome ore which consists of an altered natural ferrous chromite ore containing the greater part of its original chromic oxid content and having the greater part of its ferrous oxid content displaced by an added base and removed, said manufactured ore having the physical characteristics of a glassy material set from a molten state and being chemically basic in its nature.
2. As a new article of manufacture, an artificial chromite ore made from natural ferrous chromite ore and containing a substantial amount of lime chromite replacing the original ferrous chromite, said artificial ore being of fused glassy character and basic in its nature and having a low ratio of iron to chromium, said ratio being less than 23:77.
3. A manufactured chrome ore preparation adapted for reduction by ferrosilicon in smelting to produce low carbon ferrochromium of high chromium content which consists of an altered natural ferrous chromite ore containing the greater part of the original chromic oxid content and having the greater part of its ferrous oxid removed therefrom and replaced by lime, being of a fused glassy character and chemically basic.
4. A manufactured chrome ore preparation adapted for reduction by ferrosilicon in smelting to produce low carbon ferrochromium of high chromium content which consists of an altered natural chrome ore of the ferrous chromite type containing the greater part of its original chromium oxid content and having substantially all its iron oxid removed therefrom and containing calcium chromite replacing the original ferrous chromite, being of a fused glassy character and chemically basic.
5. The process of treating natural ferrous chromite ore for production of an artificial ore with a heightened ratio of chromium to iron and with production of metallic iron as a byproduct which comprises continuously fusing such an ore in the presence of sufficient added base to displace a substantial amount of the ferrous oxid in combination with chromic oxid, reducing the displaced ferrous oxid to metal and separating the metal from the fused melt, whereby a melt is obtained rich in chromite of the added base, low in iron and of basic nature.
6. The process of claim 5 wherein the reduction of iron oxid to metal is effected by carbon.
7. In the utilization of natural ferrous chromite

ores for making chromium metal and chromium alloys, the continuous process of producing an artificial ore with a heightened ratio of chromium to iron with a byproduct of metallic iron low in chromium which comprises fusing the natural ore mixed with a sufficient quantity of an added base to displace the iron oxid in the ore from combination with chromic oxid, selectively reducing the displaced iron oxid so as to form separable masses of molten iron metal and overlying fluxed ore, sufficient iron being displaced from the ore and reduced to raise the ratio of chromium to iron in the treated ore above 77 to 23 and to increase the percentage of chromium in the ore.

8. A process of utilizing natural chrome iron ore in producing chromium metal and alloys of high chromium content which comprises continuously melting said ore with a fluxing base in contact with a reducing agent, the quantity of reducing agent and base, the temperature and the time of contact being about sufficient to reduce the iron of the ore selectively and in a molten condition and to leave unreduced the greater part of the Cr_2O_3 in the ore, removing the reduced molten iron and thereafter reducing the ore melt to obtain metal high in chromium.

9. In the process of claim 8, selectively reducing and removing substantially all the contained iron from the ore melt and thereafter reducing chromium from the ore melt with ferrosilicon to obtain carbon-free ferrochromium.

10. In the process of claim 8, selectively reducing and removing substantially all the iron from the ore melt and thereafter reducing chromium from the ore melt with 50 per cent ferrosilicon in such proportion as to obtain low carbon ferrochromium containing over 70 per cent chromium.

11. In the process of claim 8, selectively reducing and removing substantially all the iron from the ore melt and thereafter reducing chromium from the ore melt with silicon in such proportion as to obtain metallic chromium.

12. In the manufacture of chromium alloys from chrome iron ores, a process which comprises continuously melting the ore in an electric furnace in the presence of a reducing agent and an added base in such quantities as to produce an underlying layer of molten metal high in iron and low in chromium and an ore melt containing a chromite of the added base and a lowered ratio of iron oxid, separating the molten metal from the ore melt and thereafter reducing the ore melt to obtain metal high in chromium and low in iron.

13. In the alteration of natural chromite ore to produce an artificial ore of heightened chromium content adapted for use in making chromium metal and alloys of high chromium content, the process which comprises continuously fusing the natural ore in an electric furnace mixed with an added base, thereby displacing FeO from the chromite, fusion being at a chromium reducing temperature and with an amount of carbon about that required for the reduction of iron alone, and removing the molten iron thereby produced.

14. The process of treating ferrous chromite ore with production of an artificial ore having a higher ratio of chromium to iron and with production of metallic iron low in chromium as a byproduct which comprises continuously fusing such an ore in a submerged arc furnace and in the presence of sufficient base to flux the chromite and to displace a substantial amount of the ferrous oxid of the chromite and form a glassy melt, simultaneously reducing the displaced ferrous oxid to metal and separating the metal from the

fused melt so as to obtain a melt rich in chromite of the added base, low in iron and of basic nature.

15. The process of making calcium chromite which comprises fusing a mixture of chromite ore with an amount of CaO sufficient to replace the FeO present, reducing the FeO to metallic iron and separating the metal and the fused calcium chromite.

16. A process which comprises heating a charge mixture comprising lime and chrome ore containing ferrous chromite to produce a molten product comprising calcium chromite formed by substitution of calcium oxide for ferrous oxide of chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable product high in calcium chromite, and separating the metallic iron product and the calcium chromite product.

17. A process which comprises heating a charge mixture comprising lime and chrome ore containing ferrous chromite to produce a molten product comprising calcium chromite formed by substitution of calcium oxide for ferrous oxide of chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable calcium chromite product, having a higher Cr:Fe ratio than the original ore and a Cr_2O_3 content of the same order as that of the original ore, and separating the metallic iron product and the calcium chromite product.

18. A process which comprises forming a charge mixture comprising chrome ore containing ferrous chromite and a basic compound capable of substituting for the ferrous oxide of the ferrous chromite to displace the ferrous oxide from chemical combination with the chromic oxide of the ferrous chromite and form altered or substituted chromite, heating the charge mixture to produce a molten product comprising altered or substituted chromite formed by substitution of the basic compound for ferrous oxide of the chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable product high in altered or substituted chromite, separating the metallic iron product and the altered or substituted chromite product, and separately reducing the altered or substituted chromite product to produce metal predominating in chromium.

19. A process which comprises heating a charge mixture comprising lime and chrome ore contain-

ing ferrous chromite to produce a molten product comprising calcium chromite formed by substitution of calcium oxide for ferrous oxide of chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable product high in calcium chromite, separating the metallic iron product and the calcium chromite product, and separately reducing the calcium chromite product to produce metal predominating in chromium.

20. A process which comprises heating a charge mixture comprising lime and chrome ore containing ferrous chromite to produce a molten product comprising calcium chromite formed by substitution of calcium oxide for ferrous oxide of chromite, reducing ferrous oxide thereby displaced to produce a metallic iron product and a separable calcium chromite product, having a higher Cr:Fe ratio than the original ore, separating the metallic iron product and the calcium chromite product, and separately reducing the latter to ferrochromium.

21. The process of making a synthetic ore adapted for the production of commercial ferrochromium from a natural ferrous chromite ore containing a chromium:iron ratio lower than 70:30, which comprises heating a charge of such ferrous chromite ore to produce a molten product containing calcium chromite formed from ferrous chromite of the ore in the presence of sufficient lime and a sufficient amount of reducing agent to convert enough of said ferrous chromite to calcium chromite to give said molten product a chromium:iron ratio of at least 70:30, and to reduce to metallic form iron liberated from the converted ferrous chromite, while reducing a relatively small amount of Cr_2O_3 , and separating a metallic iron product, low in chromium, and a molten ore product, rich in calcium chromite, thereby obtained.

22. In a process for producing chromium-bearing metal involving a reduction treatment of a charge containing a chromium compound, the improvement which comprises employing for the reduction treatment a charge comprising chromite ore altered artificially by the substitution of calcium oxide for ferrous oxide chemically combined in the original ore and having a lower ratio of iron to chromium than the original ore.

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