

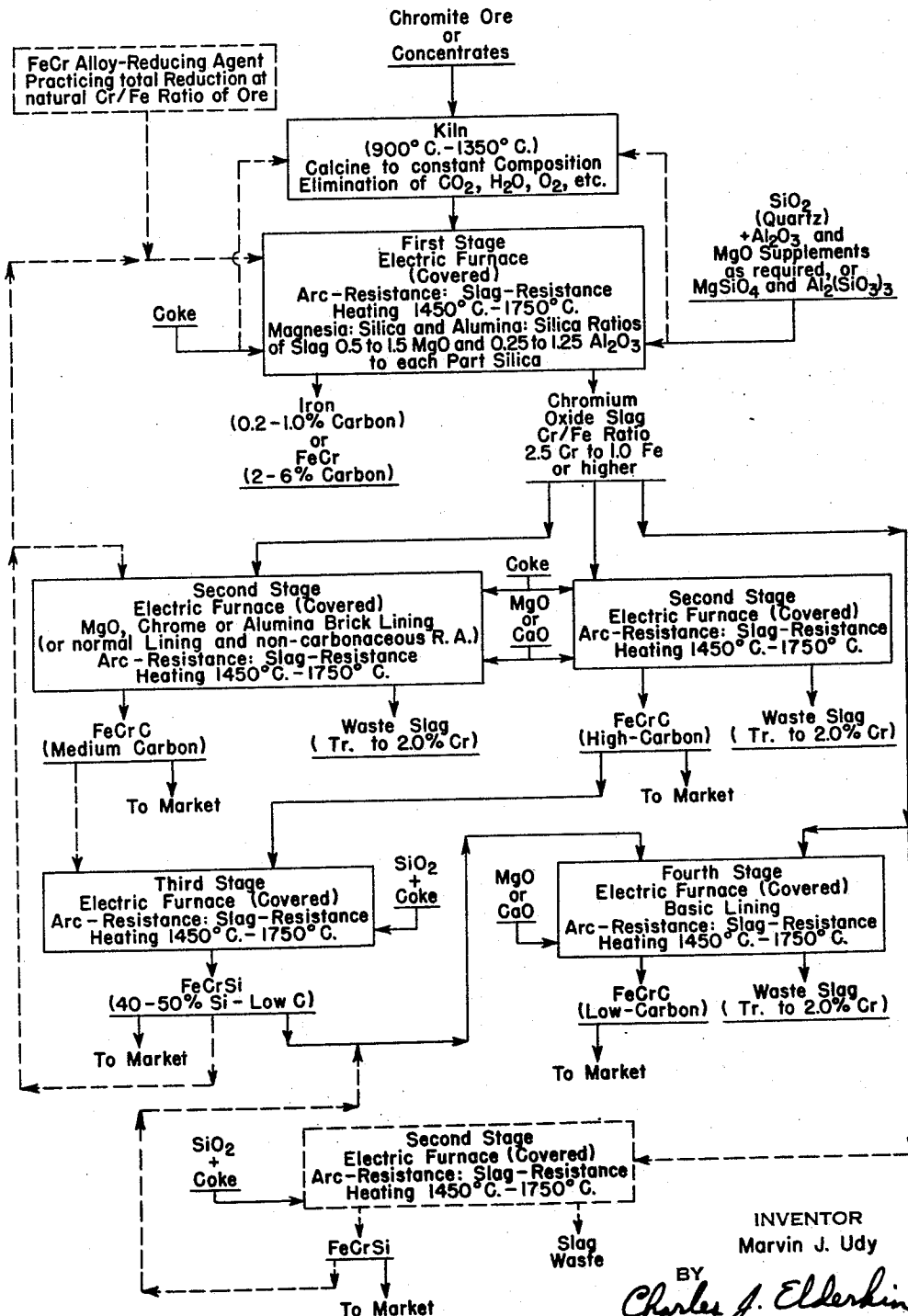
April 26, 1960

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2,934,422

PROCESS FOR THE PRODUCTION OF FERROCHROMIUM PRODUCTS

Filed April 30, 1958



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PROCESS FOR THE PRODUCTION OF FERRO-CHROMIUM PRODUCTS

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Application April 30, 1958, Serial No. 731,993

18 Claims. (Cl. 75—11)

This invention relates in general to an improved metallurgical process. More particularly, the invention contemplates the provision of an novel process which can be employed advantageously and economically to produce high-grade ferrochromium products from various grades of chromium ores and concentrates, including the usual high-grade commercial ores, and ores and concentrates which are considered of too low grade for treatment on a commercial basis by means of heretofore customary practices.

In the smelting of refractory ores such as chromite ores according to conventional techniques, it is extremely difficult to establish and maintain molten a bath of the ore of any substantial volume. Consequently, the slags produced in such smelting operations are usually so viscous as to prevent ready settling-out of small particles of metal, including iron and chromium produced during reduction, and small particles of unreduced chromite dispersed therein. In operating with slags of such high viscosity, and, in an attempt to mitigate the excessively high chromium losses that might otherwise result from discarding the slags with their entrained chromium contents, at least some existing installations deliberately avoid the addition of large quantities of fluxing agents to a reduction charge, with the object of producing the least possible quantity of slag for subsequent treatment by concentration techniques for recovery of the additional chromium values present therein. Alternatively, it has been proposed heretofore to produce controlled, relatively lower viscosity slags, i.e., slags which are diluted with respect to their refractory chromic oxide content, through the addition of relatively large quantities of calcium oxide or lime to a natural chromite ore or concentrate undergoing reduction within an electric furnace. It has been applicant's experience, however, as a result of extensive smelting operations conducted with such high-lime chromium slags, that in spite of the improved viscosities obtainable by the lime additions, the resulting slags are puffy and tend to chill extremely rapidly. In addition, the settling-out of the entrained chromium values is quite difficult to accomplish with such slags, requiring higher operating temperatures, and seldom exceeding separations of less than six percent (6.0%) Cr_2O_3 within the final residual slag product. By reason of the fact that substantial quantities (6 to 10%) of the chromium content of a chromite ore or concentrate cannot be freed from the slag burden in accordance with present smelting techniques, the production of ferrochromium products of standard grades, containing, for example, sixty-eight to seventy-two percent (68–72%) chromium, requires the use of chromite ores and concentrates containing chromium and iron in a ratio not substantially lower than about three parts chromium to each part iron by weight. This restriction, in turn, prevents the utilization of abundant sources of low-grade chromite ores in the production of commercially desirable ferrochrome products.

The present invention is based, in part, upon my discovery that substantially improved recoveries of chromium can be obtained in the smelting of chromite ores and concentrates by modifying conventional practices

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through controlled fluxing and dilution of the ores and concentrates with silica in the production of the smelting charge. Thus, I have found that contrary to generally accepted operating procedures, by avoiding the addition of calcium oxide or lime to a chromite ore or concentrate undergoing smelting for reduction and removal of iron, and employing silica as the principal added fluxing agent in conjunction with magnesium oxide and alumina naturally present within the ore or concentrate, or added thereto as such, provided the ore or concentrate is deficient in magnesium oxide and/or alumina contents, or in the form of an alumina- or magnesia-containing mineral concentrate or tailing, or in chemical combination with the silica flux in the form of a natural magnesium or aluminum silicate, such as to provide for the production of a chromic oxide slag containing magnesia, alumina and silica in respective proportions within the ranges of 0.5 to 1.5 parts by weight of magnesia (including any CaO calculated to MgO equivalency) and 0.25 to 1.25 parts by weight of alumina to each part by weight of silica, I am able to effect subsequent improved recoveries of chromium at substantially the same operating temperatures, obtaining ultimate residual slag products which are "scrubbed" of chromium values to as low as trace quantities. Preferably, the alumina-magnesia-silica ratio of the alumina-magnesia-silica-chromic oxide slag systems of the invention is adjusted as required to provide approximately equivalent parts by weight of alumina, magnesia and silica, or a 1:1:1 ratio of these components, with any calcium oxide naturally present within the ore or concentrate being calculated to magnesium oxide equivalency and considered as part of the total MgO requirements. By reason of the substantially complete chromium recoveries realized in accordance with a process of the invention, it is possible to produce standard grade ferrochromium products through the use of chromite ores and concentrates containing chromium and iron in a ratio not greater than about 2.5 parts chromium to 1.0 part iron, thus making available for processing the tremendous sources of chromite heretofore considered to be of sub-standard grade because of Cr:Fe ratios lower than 3 to 1. As applied to conventional high-grade ores and concentrates (48% Cr_2O_3), the use of an approximate 1:1:1 ratio of alumina, magnesia and silica renders it possible to effect substantially complete reduction and recovery of the chromium content of such ores within a single stage smelting process, with close control of the carbon content of the end-product ferrochromium alloy.

The process of the invention is based on my observations that certain naturally occurring high-iron chromium materials which contain little or no calcium oxide, but which do contain varying proportions of alumina, magnesia and silica, tend, most unexpectedly, upon direct smelting under controlled conditions, and in the absence of any other flux, to produce excellent slags of high chromic oxide content from which iron can be reduced and separated far more readily than from the high-lime slags which are produced deliberately in accordance with conventional practices. In addition, based on limited results obtained initially with such furnace burdens of natural composition, I have found that any high-iron chromium ore or concentrate can be adjusted to an optimum composition by the simple addition of silica and/or magnesia and alumina to provide fluid, workable synthetic slags of the desired magnesia-alumina-silica content, which can be brought readily to high chromium:iron ratios by the selective reduction and subsequent complete removal of any portion of their natural iron content. As illustrated within the examples presented hereinafter, the unique fluxing techniques of my invention have been demon-

strated in connection with an unaltered natural chromite ore of satisfactory magnesia-alumina contents which was adjusted to proper operating slag-consistency by the simple addition of silica. Chromite concentrates prepared from quantities of the same ore by the preliminary separation of silica and magnesia and lesser amounts of alumina, among other components, and intended for use in conjunction with conventional high-lime smelting practices, could be readily reconstituted to proper operating consistency in accordance with the principles of my invention by the simple addition of equivalent amounts of added silica in combination with quantities of the silica-magnesia-alumina tailings remaining from the concentration treatment. In the same manner, furnace charges consisting of such concentrates and synthetic slag additions in the form of silica, alumina and magnesia in respective amounts as required to establish within the resulting slag the desired silica-alumina-magnesia relationship specified above, have been smelted with the same high efficiencies as were obtained with the natural ore or with the concentrates reconstituted by the addition of the silica-magnesia-alumina tailings produced in concentrating the natural ore.

In accordance with one aspect of the process of my invention, a natural chromite ore or concentrate of relatively low Cr:Fe ratio is beneficiated for ultimate use in the production of ferrochromium alloys by an initial smelting operation conducted for the selective reduction and removal of excess iron present in the ore or concentrate, with the production and recovery of metallic iron of controlled chromium content, and a molten slag product of relatively enriched chromium oxide content and containing iron in any desired proportion lower than that of the original raw charge material. Thus, if desired, the initial smelting operation with high iron chrome ores can be controlled to produce an iron product containing approximately 5% chromium (chromesteel), or iron containing 10-12% or 18-20% chromium, or steel, or high-chromium irons containing 25% or more chromium, with the balance of the chromium and iron being recovered within a subsequent stage or stages as ferrochrome alloys of standard grade. In essence, the initial smelting operation is conducted to adjust the chrome:iron ratio within the slag to any desired value according to the exact nature of the ferrochrome alloy sought to be recovered within a subsequent smelting operation conducted with the chromium-enriched or iron-degraded slag recovered from the first stage, while at the same time placing the chromium oxide values present in the slag in condition for substantially complete reduction and settling-out or recovery of the metallic chromium from the ultimate waste slag product produced in said subsequent smelting operation. To this end, the natural chromite ore or concentrate is charged to a first stage electric furnace together with carbonaceous reducing material in an amount sufficient to effect reduction to the metallic state of the excess iron oxide contained therein, and silica in an amount sufficient to provide for the production of a silica-magnesia-alumina-chromium oxide slag containing silica, magnesia and alumina in respective proportions within the range specified hereinbefore; the magnesia and alumina contents thereof being derived directly from the chromite ore or concentrate, or being added to the furnace charge as required to satisfy the silica:magnesia and silica:alumina ratios, either in the form of synthetic or natural alumina- and/or magnesia-containing burdens, or in chemical combination with the silica flux as aluminum or magnesium silicate mineral. If dolomite is employed to supply the magnesia requirements of the unique slag systems of the invention, its calcium oxide content is calculated to MgO equivalency. It is found that silica-magnesia-alumina-chromium oxide slags of this type possess excellent handling properties such as fluidity, settleability, etc., and can be smelted and reduced at controlled temperatures for substantially com-

plete reduction and recovery of their chromium contents, and with equivalent power consumption as required in conventional chrome reduction operations.

In actual practice for the removal of excess iron from a natural chromite ore or concentrate, I prefer to employ a carbonaceous reducing agent such as coke within the initial smelting furnace, but a non-carbonaceous reducing agent can be employed in conjunction with the novel fluxing practices described above. Thus, in treating chromite ores which are somewhat deficient in chromium content, it may prove advantageous to employ a ferrochromium alloy or ferrochromium silicon alloy as reducing agent for the additional purpose of upgrading the resulting slag with respect to chromium oxide content. For example, such a reducing agent can be produced readily by simply smelting quantities of the natural ore or concentrate under conditions of total reduction to obtain "off-grade" ferrochromium of a composition corresponding to the natural chrome:iron ratio of the ore or concentrate, which may then be utilized as the reducing agent for the selective reduction of additional quantities of the ore or concentrate within the first stage.

The silica-magnesia-alumina-chromic oxide slag produced in the initial smelting operation, containing chromium and iron in a ratio of 2.5 parts chromium to 1.0 part iron, or higher, may be charged in the molten state, or after cooling and crushing, to a second furnace in which it is smelted in the presence of a controlled amount of added carbonaceous reducing agent or non-carbonaceous reducing agent, and controlled amounts of added basic fluxing material, if required, preferably in the form of magnesia and in an amount sufficient to provide for the eventual production of a basic residual waste slag, to produce a ferrochromium alloy of high, medium or low-carbon content. As a general rule, provided the chromite ore is fluxed initially to provide a magnesia-alumina-silica ratio of approximately 1:1:1, no further flux additions of any type are required within subsequent smelting stages of my process.

In utilizing the silica-magnesia-alumina chromium oxide slag from the first stage for the production of a high-carbon ferrochromium alloy within the second stage, the slag is charged to the second furnace together with any added basic fluxing material that might be required and sufficient coke to provide for total reduction of the iron oxide and chromic oxide contents thereof. While I also prefer to employ magnesia as a basic fluxing agent within all smelting stages subsequent to the initial iron removal stage because of the excellent handling and settling properties of the resulting silica-magnesia-alumina slags, these stages at least can be operated, if necessary, with calcium oxide, lime, limestone or dolomite as the added basic fluxing material. In operating the subsequent stages with magnesia flux, any such additions are carefully controlled to provide for the eventual production (following reduction) of a residual waste slag containing from 1 to 2 parts base to each part acid (silica), and preferably about 1.5 parts base to 1 part acid. If calcium oxide or dolomite must be employed in the subsequent stages, the additions are controlled to provide for the production of a waste slag product having a base:acid ratio of 2 to 1, i.e., a maximum of 2 parts base for each part acid.

I have found that a satisfactory commercial grade of medium-carbon ferrochromium can also be produced within a two-stage operation employing coke as the reducing agent. Thus, by smelting quantities of the chromium oxide slag produced in the first stage within a second furnace fitted with a non-carbonaceous lining such as magnesite (MgO), chrome or alumina brick, in the presence of added basic fluxing material, preferably in the form of magnesia, I am able to employ a carbonaceous reducing agent and maintain the carbon content of the ferrochromium alloy thus produced to within medium-carbon specifications solely through control of the carbon additions available from the reducing agent.

In a similar manner, when conducting the initial first-stage iron removal operation within a furnace having a carbonaceous lining, it is sometimes difficult to obtain a metallic iron product which is substantially free of metallic chromium, and a magnesite, chrome brick or alumina brick lining may be employed within the first stage to maintain a low chromium content within the iron product recovered therein. Furthermore, when the first stage reduction is practiced for the production of a ferrochromium alloy rather than metallic iron, a non-carbonaceous lining within the furnace permits one to obtain carbon control of the order of 1 to 2% within the ferrochromium product thus produced.

In the production of low-carbon ferrochromium alloys, I prefer to operate the first and second stages for the production of a high-carbon ferrochromium alloy in the manner described above, subjecting this product to a third stage smelting operation in the presence of added silica and reducing agent to produce a ferrochromium silicon product of relatively low-carbon content and a silicon content of approximately fifty percent (50%). I then charge this product as reducing agent to a fourth furnace together with additional quantities of the chromium oxide slag produced in the first stage and added magnesia (or calcium oxide) flux to effect reduction of the chromium oxide and iron oxide present in the slag with the production of a low-carbon ferrochromium alloy and a waste slag product. While this four-stage process represents preferred operating procedure from the standpoint of overall power consumption in the production of low-carbon alloy, I may treat quantities of the beneficiated slag recovered from the first stage by smelting in the second stage under such conditions as to produce ferrochromium silicon directly, rather than proceeding from the high-carbon ferrochromium to the ferrochromium silicon in three stages. The ferrochromium silicon thus produced would then be utilized within a third furnace for reduction of beneficiated slag from the first stage in the production of low-carbon ferrochromium. In a similar manner, whereas the above-described two-stage process for the production of medium-carbon ferrochromium, utilizing a carbonaceous reducing agent within a non-carbonaceous lined second-stage furnace for the reduction of beneficiated slag from the first stage, represents preferred operating procedure, I can operate in two stages directly from the beneficiated slag, or, in three stages from a high-carbon ferrochromium alloy, to produce a ferrochromium silicon product of silicon-carbon content ideally suited for the production of medium-carbon ferrochromium (18% Si), employing this product within a third or fourth stage with additional quantities of chromium oxide slag in the production of medium-carbon alloy. Of course, the ferrochromium silicon products produced by the process of the invention may be marketed directly, or recycled for use as a chromium-enriching reducing agent in the initial smelting operation.

It is believed that the foregoing process measures may be best understood by reference to the accompanying drawing wherein the single view constitutes a schematic flow diagram or flow sheet illustrating the exact sequence of steps or operations involved in a preferred process of the invention, and wherein the various alternative practices described above have been depicted by means of dotted-line indications.

In carrying out a preferred process of my invention, a further important feature thereof resides in the preliminary treatment of the chromite ores or concentrates for purposes of providing a reduction charge to the first stage of substantially constant composition. Thus, I have found that it is essential for subsequent selective reduction in the smelting stages of the process that the chromium-bearing material be stabilized to a substantially constant composition by removal of all water, the labile oxygen from CO_2 , H_2O , etc. For this purpose,

I heat the raw chromium-bearing material in a rotary kiln or other suitable piece of equipment, prior to the initial reduction step, to a temperature within the range 900°C . to 1350°C . in order to stabilize it to a constant composition with respect to oxygen content and thereby obtain better control of reduction. In addition, for economy of power, whenever possible, I prefer to conserve the sensible heat imparted to a furnace burden during a particular smelting operation by transporting intermediate products to subsequent stages without cooling, thereby conserving power that might otherwise be expended in bringing the product from a fully cooled state to the operating temperature for the subsequent stage. Similar economies can be effected through utilization of oil-fired furnaces, such as the reverberatory type, in bringing raw materials to the operating temperatures employed within the electric smelting furnaces.

While the unique fluxing practices of the invention can be employed in conjunction with any conventional form of electric furnace smelting, I attribute a substantial portion of the overall efficiency of my process to the techniques adopted in the smelting of the various furnace charges, and prefer, therefore, to operate in all stages of the process in accordance with the smelting techniques and principles which are described and claimed in my copending application Serial Number 553,645 of December 16, 1955, entitled, "Electric Furnace and Process of Operating the Same." That is to say, in conventional electric furnace smelting, the furnaces are designed and operated as submerged arc furnaces, in that, the actual arcing tips of the furnace electrodes are submerged with respect to the raw charge, distances ranging from four to ten feet (4-10'). In this type of smelting, segregation of the reducing agent and fines in the charge takes place quite readily with the result that the reducing agent collects under the electrodes and raises the electrodes at any given voltage, thereby lengthening the arcs with the development of very high localized temperature zones, causing over-reduction and volatilization of charge components and unpredictable or inefficient operation as a whole. Furthermore, it is virtually impossible to employ fine ores to any extent in such smelting operations, but rather, the ores must be carefully classified to insure delivery to the furnace of lump-type charge containing on an average of not more than twenty-percent (20%) of minus twenty (-20) mesh particle size ores, in order to prevent excessive dust losses by reason of fines being carried out of the furnace chamber under action of pressurized gases produced adjacent the electrode tips beneath the relatively deep-bed or cover of raw charge which surrounds the electrodes.

The furnace design and smelting technique of my aforementioned copending application are based on the discovery that operation of an arc electric furnace with the electrode tips carried on the surface of a molten slag bath within the furnace, or, with a maximum of one-half inch ($\frac{1}{2}$ ") arcs extending to the surface of the slag bath to a limited submergence of the arcing tips to a depth of three inches (3") within the slag bath, such as to avoid wetting of the electrodes with molten slag, not only prevents segregation of the charge components but permits much more power to be supplied to the furnace at lower operating voltages, and the smelting temperatures can be held constant within very close tolerances. Furthermore, the charge can be of much finer particle sizes, and, in fact, concentrates are preferable, and still there are practically no dust losses since the avoidance of deep columns of raw charge material adjacent the electrodes effectively eliminates high-pressure zones of the type developed in prior conventional smelting operations. As described in my copending application, the preferred furnace design employed in practicing the foregoing smelting technique is largely determined by the principles applied, in that, the width of the furnace chamber is controlled such as to avoid adherence of slag to the walls

of the furnace and the height of the chamber is a function of the desired angle of repose of charge material within the furnace, such as to avoid submergence of the arcing tips within raw charge material. In actual practice, I have found that an angle of repose of charge material of about forty-five degrees (45°) is quite effective for most purposes with the charge being fed down the banks or side walls of the furnace in such manner that the natural angle of repose of the material being smelted will just reach the center of the furnace with the raw charge resting or floating upon the molten slag bath, while depressing the peripheral portions of the slag bath to avoid adherence of slag to the furnace walls. Smelting takes place under the raw charge and within the first six (6) to eight (8) inches of charge material floating on the slag and produces but a minimum of heat losses by radiation to the roof of the furnace. For the most part, the reaction zone of the furnace is controlled through control of the rate of feed of raw charge to provide for the maintenance of a substantially constant-depth slag bath thereby insuring a substantially constant-resistance current path, and the overall effect is the establishment of combined arc-resistance, slag-resistance heating with the transfer of heat taking place from the slag to the smelting charge in lieu of the conventional arc-coke resistance heating which characteristically occurs in prior submerged arc smelting practices. Furthermore, segregation of coke is completely eliminated since the electrodes are maintained clear of the reducing charge.

In general, the smelting temperatures employed in the practice of my invention will fall within the range of from 1450° C. to 1750° C. In the first stage of smelting for iron removal, the relatively high chromium oxide content of the slags requires smelting temperatures of the order of 1650 to 1750° C., with preferred operating temperatures being about 1690–1700° C. In subsequent stages for the production of ferrochromium, owing to the fact that the Cr₂O₃ is substantially eliminated from the slags, it is found that satisfactory operating temperatures will usually be of the order of 1450–1550° C.

For the most part, the power consumption will be dependent to a considerable extent on the total Cr₂O₃ content left in a beneficiated slag. By suitable partitioning of the chromium content available within an ore or concentrate between the metallic product produced in the first stage and the residual chromium oxide slag, it is possible to concentrate the slags for any grade of ore to optimum values. Usually, I find it to be most desirable to adjust the Cr₂O₃ content of the beneficiated slags to values within the range of from 23% to 30%.

It is found that the metallic iron removed from a high-iron chrome ore can be controlled with respect to carbon content to values as low as 0.20–1.0%. Carbon control in the medium-carbon and high-carbon ferrochromium is readily obtained at values within the range of 1.5–5.0%, or 2.0–6.0% for single stage operations with high-grade ores. Metal of 11 to 12% chromium and 0.3% carbon, for example, can be readily produced in the first stage of smelting and needs but a slight degree of refining and carbon and alloying additives to yield cutlery-grade steel. In a similar manner, an 18 to 20% ferrochromium product of low carbon content needs only slight refining and nickel added to produce stainless steel.

The following analysis is typical of the low Cr/Fe ores which can be treated in accordance with the principles of the invention:

(A) Chromite ore analysis (calcined):		Percent
Fe	-----	13.73
Al ₂ O ₃	-----	9.16
MgO	-----	27.00
CaO	-----	3.42
SiO ₂	-----	22.90
P	-----	Trace
S	-----	-----
Cr ₂ O ₃	-----	20.1

As pointed out hereinbefore, the process of the invention is also applicable to the treatment of chromite ore concentrates such as that represented by the analysis presented below. The particular concentrate illustrated was prepared by treatment of a chrome ore of the foregoing analysis.

(B) Chromite ore concentrates:		Percent
Fe	-----	15.93
Al ₂ O ₃	-----	14.9
MgO	-----	15.71
CaO	-----	0.57
SiO ₂	-----	7.70
P	-----	0.016
S	-----	0.011
Cr ₂ O ₃	-----	38.57

In prototype operations conducted in accordance with the process of the invention, I have found that tailings of the following analysis, obtained as a waste product in the preparation of the foregoing concentrates, represent a relatively abundant and inexpensive source of magnesia, alumina and silica for practicing the unique fluxing techniques detailed hereinbefore, serving at the same time to introduce additional chromium into the resulting slags.

(C) Tailings analysis:		Percent
Fe	-----	9.42
Al ₂ O ₃	-----	3.80
MgO	-----	35.2
CaO	-----	3.70
SiO ₂	-----	37.06
P	-----	Trace
S	-----	-----
Cr ₂ O ₃	-----	6.90

The following examples illustrate the specific application of the foregoing principles and objects of the invention to the treatment of ores and/or concentrates of the analyses set forth above, in conjunction with fluxing materials of various types:

EXAMPLE I.—(NATURAL ORE)

Calcined chromite ore of the analysis (A) set forth above in amount 100 pounds, was charged to an electric furnace of the type described in my afore-mentioned copending application Serial No. 553,645, together with 15 pounds of silica in the form of quartzite, and 5½ pounds of coke (85% F.C.), and smelting at temperatures within the range 1450–1750° C. under action of combined arc-resistance, slag-resistance heating to yield ten (10) pounds of a metallic iron product containing two percent (2%) chromium, and a chromium oxide slag which analyzed as follows:

Cr ₂ O ₃	-----	18.53%.
Fe	-----	3.49%–4.47% FeO.
Cr/Fe	-----	3.63/1.
SiO ₂	-----	39.06%.
Al ₂ O ₃	-----	10.67%.
MgO	-----	21.36%.
CaO	-----	1.47%.

The above slag, in amount 100 pounds, was subsequently smelted in the same type of furnace under identical conditions of operation together with 55.5 pounds of magnesia and nine (9) pounds of coke (85% F.C.), to yield a high-carbon ferrochromium product analyzing over sixty-nine percent (69.4%) chromium, 1.04 percent silicon and five percent (5%) carbon, and a waste slag product containing 0.66 percent chromium.

EXAMPLE II.—(RECONSTITUTED ORE)

Charge proportioned on the basis of fifty (50) pounds of concentrates of the analysis (B) above, 37.5 pounds

of tailings of the analysis (C) above, ten (10) pounds of silica in the form of quartzite and 7.5 pounds of coke (85% F.C.), was supplied continuously to the furnace and smelted therein under the same conditions as described in Example I. The furnace was tapped intermittently yielding metallic iron of two percent (2%) average chromium content, and chromium oxide slag of average analysis as follows:

Cr ₂ O ₃	percent	23.59
Fe	do	4.40
Cr/Fe		3.67/1
SiO ₂	percent	32.24
Al ₂ O ₃	do	13.47
MgO	do	17.20
CaO	do	2.93

The above slag was subsequently smelted under the same furnace conditions to yield a high-carbon ferrochromium product analyzing seventy percent (70%) chromium, 1.17 percent silicon and 6 percent (6%) carbon, and a waste slag product containing 1.44 percent chromium.

EXAMPLE III.—(SYNTHETIC SLAG)

Charge proportioned on the basis of fifty (50) pounds of concentrates of the analysis (B) above, fifteen (15) pounds of magnesia, fifteen (15) pounds of silica in the form of quartzite, 1.5 pounds of alumina and 3.5 pounds of coke (85% F.C.), was supplied continuously to the electric furnace and smelted under the same conditions as described in Example I. The furnace was tapped intermittently to yield metallic iron of 1.7 percent average chromium content, and a chromium oxide slag of average analysis as follows:

Cr ₂ O ₃	percent	22.1
Fe	do	5.9
Cr/Fe		2.55/1
SiO ₂	percent	32.37
Al ₂ O ₃	do	12.67
MgO	do	18.94
CaO	do	2.03

The above slag was subsequently smelted on a continuous basis under the same furnace operating conditions to yield a high-carbon ferrochromium product averaging sixty-nine percent (69%) chromium, 1.5 percent silicon and 5.0 percent carbon, and a waste slag containing less than 1.0 percent chromium.

A quantity of slag of the same analysis was successfully smelted and reduced with ferrochromium silicon to provide a ferrochromium product analyzing 0.01% carbon content.

Quantities of this slag were also reduced with coke in a furnace provided with a fused alumina lining to provide a ferrochromium product of approximately 1.2% carbon content.

EXAMPLE IV

A Canadian chromite ore was treated on a continuous basis within a 100 kva. arc electric furnace (tilting-type) operated in accordance with the smelting techniques described hereinbefore. The average weight of the charges per heat was approximately 112 pounds, consisting of 30 pounds of the ore, 70 pounds of a concentrate from the ore, 6 pounds of silica and 6-7 pounds of coal. The analyses of the ore and concentrate are as follows.

Chromite ore (Canadian):

Cr	9.01%–13.40%	Cr ₂ O ₃
Fe	9.86%	(FeO and Fe ₂ O ₃)
SiO ₂	22.00%	
CaO	8.40%	
MgO	20.34%	
Al ₂ O ₃	11.70%	
L.O.I.	10.42%	

Concentrate:

Cr	18.50%–27.00%	Cr ₂ O ₃
Fe	17.30%–23.30%	FeO and Fe ₂ O ₃
SiO ₂	12.00%	
CaO	4.51%	
MgO	12.43%	
Al ₂ O ₃	16.41%	
L.O.I.	2.64%	

During smelting, the temperature of the slag as read with a black body radiation pyrometer averaged within the range 1650–1750° C. The furnace was tapped intermittently for recovery of separate slag and metal products. The analyses of these products for a representative group of heats are set forth in the following table:

Table I

Heat	Slag Analysis (Percent)				Metal Analysis (Percent)		
	Cr	Fe	Fe (Free)	Cr/Fe	Cr	Si	C
1	15.84	4.60	1.39	3.44	10.22	0.05	0.14
2	15.52	4.60	0.59	3.38	11.02	0.05	0.20
3	17.64	4.70	1.23	3.76	10.78	0.05	0.11
4	16.17	3.75	0.43	4.31	12.49	0.05	0.17
5	16.75	4.49	0.59	3.72	12.68	0.05	0.11
6	17.32	4.28	0.80	4.05	13.20	0.07	0.15
7	17.10	4.30	0.80	3.98	12.90	0.28	0.13
8	18.58	4.34	1.49	3.48	10.16	0.11	0.18

The following data represent average analyses for the non-metallic constituents of some of the slags from Table I:

Table II

SiO ₂	CaO	Al ₂ O ₃	MgO
27.52	6.14	15.64	18.22
28.30	6.23	16.00	17.97
25.40	6.33	16.31	17.63
28.40	6.23	15.76	18.16

This application constitutes a continuation-in-part replacement of my prior copending application Serial Number 626,146, filed December 4, 1956, now abandoned, and also entitled "Process for the Production of Ferrochromium Products."

Having thus described the subject matter of my invention, what it is desired to secure by Letters Patent is:

1. Process for the production of ferrochromium that comprises smelting a charge comprising chromite-bearing material in the presence of a reducing agent in amount sufficient to effect reduction to the metallic state of substantially all of the iron and chromium contained therein, fluxing said chromite-bearing material with silica, alumina and magnesia in respective amounts as required in combination with the natural silica, alumina and magnesia contents thereof to provide for the production of a fluid molten slag product containing silica, alumina and magnesia in respective proportions within the ranges of 0.5 to 1.5 parts by weight of magnesia and 0.25 to 1.25 parts by weight of alumina to each part by weight of silica, and separating and recovering ferrochromium from said fluid molten slag product.

2. Process for the production of ferrochromium that comprises smelting a charge comprising chromite-bearing material in the presence of a reducing agent in amount sufficient to effect reduction to the metallic state of substantially all of the iron and chromium contained therein, fluxing said chromite-bearing material with silica, alumina and magnesia in respective amounts as required in combination with the natural silica, alumina and magnesia contents thereof, and including any calcium oxide calculated to MgO equivalency, to provide for the production of a fluid molten slag product containing mag-

nesia, alumina and silica in a ratio of 1:1:1 parts by weight, and separating and recovering ferrochromium from said fluid molten slag product.

3. In a process for the production of enhanced chromium:iron ratio slag concentrates from relatively low chromium:iron ratio chromite-bearing material involving the selective reduction of a portion of the iron content of said material to provide a beneficiated slag product containing the remaining iron and substantially all of the chromium content of said material, the improvement that comprises fluxing the chromite-bearing material with added silica in combination with the natural magnesia and alumina contents thereof to provide a fluid molten slag from which the metallic iron may be settled and separated readily.

4. In a process for the production of enhanced chromium:iron ratio slag concentrates from relatively low chromium:iron ratio chromite-bearing material involving the selective reduction of a portion of the iron content of said material to provide a beneficiated slag product containing the remaining iron and substantially all of the chromium content of said material, the improvement that comprises fluxing the chromite-bearing material with silica, alumina and magnesia in respective amounts as required in combination with the natural silica, alumina and magnesia contents thereof to provide for the production of a fluid molten slag product containing silica, alumina and magnesia in respective proportions within the range of 0.5 to 1.5 parts by weight of magnesia and 0.25 to 1.25 parts by weight of alumina to each part by weight of silica.

5. In a process for the production of enhanced chromium:iron ratio slag concentrates from relatively low chromium:iron ratio chromite-bearing material involving the selective reduction of a portion of the iron content of said material to provide a beneficiated slag product containing the remaining iron and substantially all of the chromium content of said material, the improvement that comprises fluxing the chromium-bearing material with silica, alumina and magnesia in respective amounts as required in combination with the natural silica, alumina and magnesia contents thereof to provide for the production of a fluid molten slag product containing silica and magnesia in approximately equal proportions by weight and alumina in an amount within the range 0.25 to 1.25 parts by weight to each part by weight of silica, and conducting the selective reduction within an arc electric furnace provided with a noncarbonaceous lining in order to avoid reduction of any substantial amount of the chromic oxide content of said chromite-bearing material.

6. In a process for the production of a ferrochromium product from chromite-bearing material of relatively low chromium:iron ratio, the improvement that comprises passing the chromite-bearing material in the form of a calcined, substantially constant composition charge into a first covered electric furnace together with a controlled amount of a carbonaceous reducing agent, and silica, alumina and magnesia in respective amounts as required in combination with the natural silica, alumina and magnesia contents of the material to provide for the production of a fluid molten slag product containing silica, alumina and magnesia in respective proportions within the ranges of 0.5 to 1.5 parts by weight of magnesia and 0.25 to 1.25 parts by weight of alumina to each part by weight of silica; subjecting the charge to reduction smelting conditions under action of combined arc-resistance, slag-resistance heating to effect the selective reduction to the metallic state of a predetermined portion of the iron oxide content of said material with the production of molten metallic iron and molten slag containing substantially all of the chromic oxide content of the original material; separating the molten metallic iron from the molten slag; passing the molten slag into a second covered electric furnace together with added basic

fluxing material and added reducing material; subjecting the slag to reduction smelting conditions within the second furnace under action of combined arc-resistance, slag-resistance heating to effect reduction to the metallic state of substantially all of the chromic oxide contained therein and the remainder of the iron oxide content of the original material with the production of a molten ferrochromium product and molten residual slag; and separating and recovering the molten ferrochromium product from the molten residual slag.

7. The process as claimed in claim 6, wherein said second electric furnace is operated with a carbonaceous reducing agent for the production and recovery of a high-carbon grade of ferrochromium, said high-carbon ferrochromium product being charged to a third furnace with added silica and reducing material and smelted therein under combined arc-resistance, slag-resistance heating with the production and recovery of a low-carbon ferrochromium silicon product.

8. The process as claimed in claim 7, wherein said ferrochromium silicon product is charged in a controlled amount to a fourth furnace together with additional quantities of the molten chromic oxide slag recovered from the first furnace and added basic fluxing material, and smelted therein under action of combined arc-resistance, slag-resistance heating with the production and recovery of a low-carbon ferrochromium product.

9. The process as claimed in claim 8, wherein magnesia is employed as the basic fluxing material within the second and fourth furnaces and is added to the furnace charges in an amount sufficient to provide for the production of a residual waste slag product having a base:acid ratio within the range 1 to 2 parts base to each part acid.

10. The process as claimed in claim 8, wherein a material selected from the group consisting of calcium oxide and dolomite is employed as the basic fluxing material within the second and fourth furnaces and is added to the furnace charges in an amount sufficient to provide for the production of a residual waste slag product having a base:acid ratio of 2 parts base to each part acid.

11. The process as claimed in claim 6, wherein magnesia is employed as the basic fluxing agent within the second furnace and is added to the furnace charge in an amount sufficient to provide for the production of a residual waste slag product having a base:acid ratio within the range of 1 to 2 parts base to each part acid.

12. The process as claimed in claim 6, wherein a material selected from the group consisting of calcium oxide and dolomite is employed as the basic fluxing agent within the second furnace and is added to the furnace charge in an amount sufficient to provide for the production of a residual waste slag product having a base:acid ratio of 2 parts base to each part acid.

13. The process as claimed in claim 6, wherein said second electric furnace is operated with a carbonaceous reducing agent and added silica for the production and recovery of a low-carbon ferrochromium silicon product, said ferrochromium silicon product being charged to a third furnace with added basic fluxing material and additional quantities of the molten chromic oxide slag recovered from the first furnace, and smelted therein under action of combined arc-resistance, slag-resistance heating with the production and recovery of a low-carbon ferrochromium product.

14. In a process for the production of enhanced chromium:iron ratio slag concentrates from low chromium:iron ratio chromite material, the improvement that comprises heating a charge comprising the chromite material and added silica, alumina and magnesia fluxing materials within an arc electric furnace under action of combined arc-resistance, slag-resistance heating and in the presence of a controlled amount of a carbonaceous reducing agent to effect the selective reduction to the metallic state of a predetermined portion of the iron oxide content thereof,

and separating and recovering a metallic iron product of low chromium content and a slag product of enhanced chromium:iron ratio.

15. Process for the production of ferrochromium that comprises, heating a charge comprising chromite-bearing material and added silica, alumina and magnesia fluxing materials in respective amounts as required in combination with the natural silica, alumina and magnesia contents thereof to provide for the production of a fluid molten slag product containing magnesia, alumina and silica in a ratio of 1:1:1 parts by weight, within an arc electric furnace and in the presence of a controlled amount of a carbonaceous reducing agent to effect the selective reduction to the metallic state of a pre-determined portion of the iron oxide content thereof, separating and recovering a metallic iron product of low chromium content from said fluid molten slag product, and subjecting said fluid slag to further smelting without additional fluxing for the production and recovery of ferrochromium.

16. The process as claimed in claim 15, wherein said fluid molten slag product is adjusted to a Cr_2O_3 content within the range of from 23 to 30 percent by selective reduction of a portion of the chromium oxide content of the chromite-bearing material.

17. Process for the production of ferrochromium that comprises, heating a charge comprising chromite-bearing material and added silica, alumina and magnesia fluxing materials in respective amounts as required in combination with the natural silica, alumina and magnesia contents thereof to provide for the production of a fluid molten slag product containing silica, alumina and magnesia in respective proportions within the ranges of from 0.5 to 1.5 parts by weight of magnesia and from 0.25 to 1.25 parts by weight of alumina to each part by weight of silica, within an arc electric furnace and in the pres-

ence of a controlled amount of a carbonaceous reducing agent to effect the selective reduction to the metallic state of a pre-determined portion of the iron oxide content thereof, separating and recovering a metallic iron product of low-chromium content from the fluid molten slag produced, and subjecting said fluid slag to further smelting for the production and recovery of ferrochromium.

18. Process for the production of ferrochromium that comprises, heating a charge comprising chromite-bearing material and added silica, alumina and magnesia fluxing materials in respective amounts as required in combination with the natural silica, alumina and magnesia contents thereof to provide for the production of a fluid molten slag product containing silica, alumina and magnesia in respective proportions within the ranges of from 0.5 to 1.5 parts by weight of magnesia and from 0.25 to 1.25 parts by weight of alumina to each part by weight of silica, within an arc electric furnace and in the presence of a controlled amount of a carbonaceous reducing agent to effect the selective reduction to the metallic state of a pre-determined portion of the iron oxide content thereof and a controlled portion of the chromium oxide content thereof, separating and recovering an iron-chromium alloy from the fluid molten slag produced, and subjecting said fluid slag to further smelting for the production and recovery of ferrochromium.

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