Jan. 31, 1967 H. W. RATHMANN ETAL 3,301,669

PRODUCTION OF A HIGH CHROMIUM CONTAINING FERROCHROME

Filed Feb. 27, 1964 2 Sheets-Sheet 1

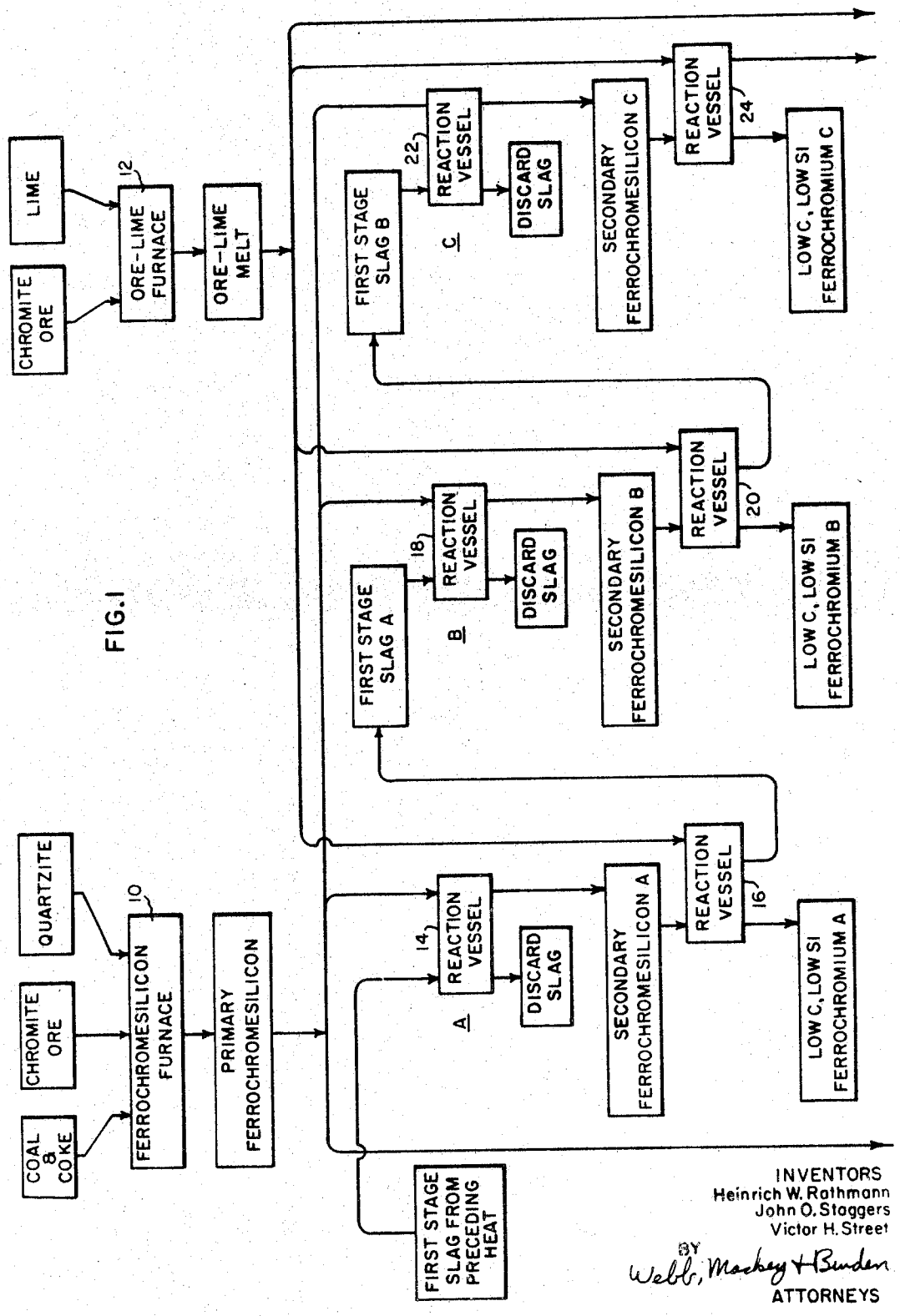


FIG. 1

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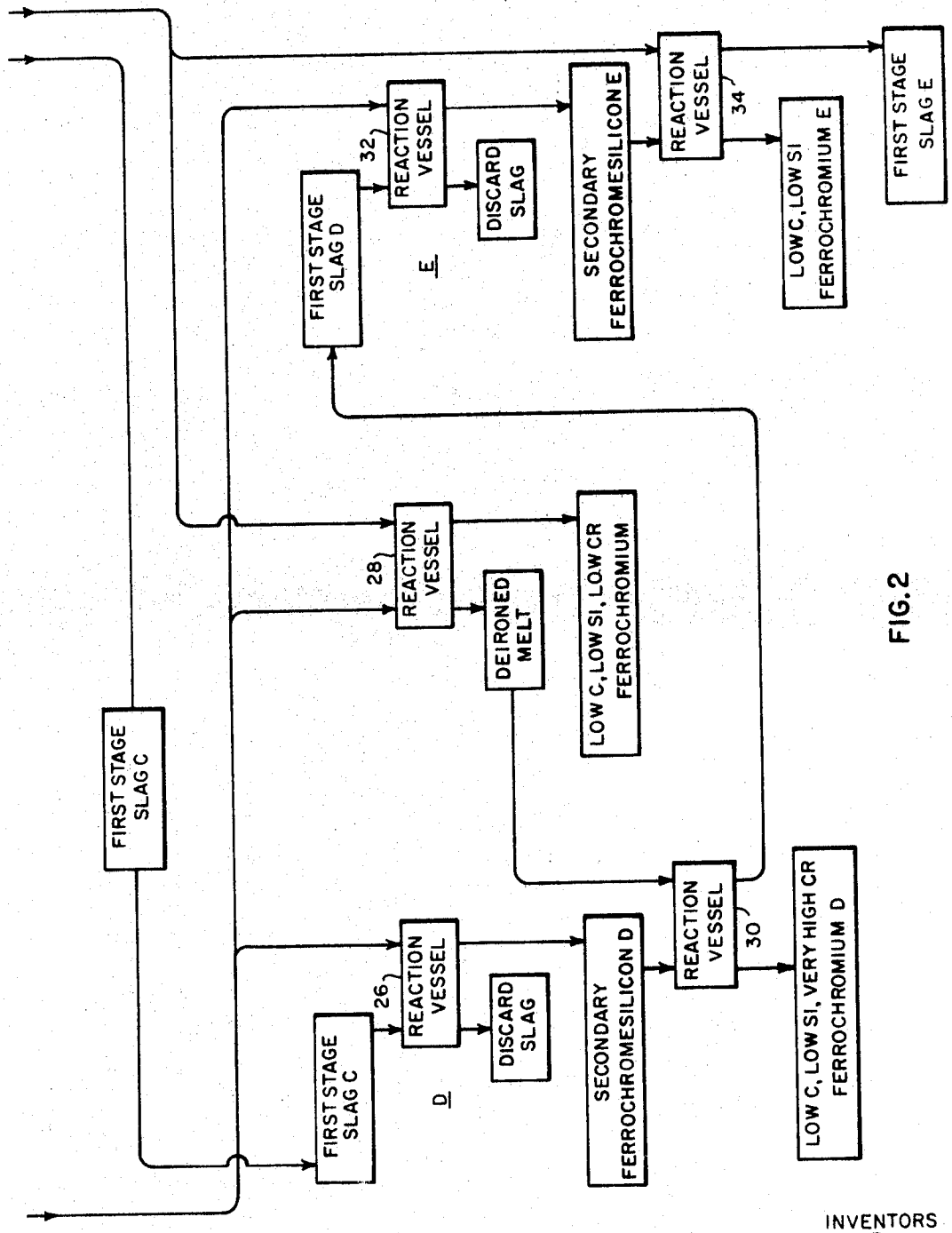


FIG. 2

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United States Patent Office

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PRODUCTION OF A HIGH CHROMIUM CONTAINING FERROCHROME

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6 Claims. (Cl. 75—130.5)

This invention relates to improvements in the production of high chromium containing ferrochromium from chromite ores and relates in particular to a new and novel method for producing particularly high chromium, low carbon and low silicon ferrochromium.

In the production of master alloys that are employed extensively to introduce chromium into high chromium content metal compositions such as super alloys, tool steels, stainless steels, etc. molten chromium containing ores, such as chromite, which contain metal constituents in the form of oxides, are treated with reducing agents to obtain molten metal alloys. Although chromium oxide is the primary constituent of the chromium bearing ores, iron oxide is invariably present. It is not possible to reduce the chromium oxide without also reducing the iron oxide present in the chromite ores so that the resultant metal is an alloy of chromium and iron that is commonly referred to as ferrochromium.

The relationship of the chromium content to the iron content or the chromium to iron ratio (Cr/Fe ratio) of a given chromite ore is of considerable importance since the ferrochromium obtained by a complete reduction of the ore will have a Cr/Fe ratio that is substantially proportional to the ratio of such elements in the ore.

The high chromium-low iron content chromite ores and particularly ores that exhibit high Cr/Fe ratios are quite naturally in great demand because these ores yield a ferrochromium of high chromium and low iron content. The lower the iron content of a given ferrochromium master alloy, the less need be taken into account when the ferrochromium is employed to introduce the chromium into alloy compositions. Also, a particularly high chromium content ferrochromium is a necessity where the addition is for the purpose of providing chromium in the production of an alloy composition having a particularly high Cr/Fe ratio. For example, a superalloy containing 8% chromium and 2% iron (plus W, Co, Mo, etc.) must be made by using a ferrochromium of at least 80% chromium.

It is well known that the Cr/Fe ratio of chromite ores may be increased by selective reduction of the iron oxide. Such ore beneficiation is predicated on the fact that when reducing agents, such as carbon and silicon, are added to molten chromite ores in relatively small quantities or amounts (i.e., that required to react stoichiometrically with 10%, 20% or 30% of the metal oxides of the ore) the iron oxide is reduced preferentially to the chromium oxide. In such selective reductions, a substantial portion of the chromium in the ore being beneficiated by selective reduction is unavoidably reduced and combines with the reduced iron. Thus, a substantial portion of the chromium is lost insofar as production of useable ferrochromium is concerned. Some of the low chromium-high iron alloy produced during the selective reduction or beneficiation is retained as fine metallic shot (metal particles) imbedded in the up-graded slag. This metallic shot must be removed to prevent a down-grading of ferrochromium produced from this slag. The slag must be

cast, crushed and subjected to magnetic separation to remove the imbedded shot prior to reduction. The added costs of such selective reduction render such operation uneconomical, particularly in view of the substantial loss of chromium in the high iron ferrochromium alloy produced during the selective reduction step.

An example of selective reduction is taught by United States Patent 2,098,176, Udy, and a method for removing chromium shot by crushing and magnetic separation is taught by the United States Patent 2,448,882, Greffe.

The only other commercially available source of chromium is electrolytic chromium which is prohibitively expensive.

A consideration which must be taken into account in the production of ferrochromium is the contaminating elements introduced by the reducing agents employed. For example, one common reducing agent is carbon; however, when carbon is used the resulting ferrochromium will possess a relatively high carbon content which is undesirable since many, if not most, of the alloys for which high chromium content ferrochromium is in demand must possess low carbon contents. It is difficult to remove carbon from ferrochromium once introduced, since further oxidation of the molten bath after the formation of the ferrochromium tends to remove chromium along with carbon.

Another common reducing agent is silicon, usually introduced in the form of ferrochromesilicon. The use of this element provides a ferrochromium of a particularly desirable low carbon content; however, if used in such quantities as to effect a substantially complete reduction of the chromite ore, the silicon content of the resultant ferrochromium is undesirably high. If the quantity of silicon used as a reduicng agent is kept below that amount which will effectively reduce substanitally all of the metal oxides present, chromium values of the ore are lost in the slag.

A particularly desirable procedure (taught by United States Patent 1,543,321, Danieli) in common usage for reducing chromite ores to produce low carbon, low silicon ferrochromium so as to obtain the maximum benefit from the chromium iron ratio of the chromite ores is a two-step process wherein:

Step (1).—A ferrochromesilicon alloy having a relatively high silicon content (referred to as primary ferrochromesilicon) is oxidized by a molten slag from a preceding heat (a first stage or intermediate slag) which contains a moderate percentage of chromium oxide. This reaction results in the formation of a ferrochromesilicon alloy of reduced silicon content (referred to as a secondary ferrochromesilicon) and a slag that is extremely low in chromium oxide content and which may be discarded (discard slag), and

Step (2).—The secondary ferrochromesilicon (of reduced silicon content) from Step (1) is oxidized by a molten slag containing a relatively high percentage of chromium and iron oxide (referred to as the chrome ore-lime melt). This reaction results in the formation of a low carbon, low silicon ferrochromium and a first stage or intermediate slag (to be used in a subsequent heat).

The term "stage" is used herein to distinguish the two stage reduction of the chrome ore-lime melt from the two step oxidation of the ferrochromesilicon. The two step oxidation of ferrochromesilicon is set forth above. In this countercurrent cyclic process the two stage reduction of the chrome ore-lime melt is in the opposite direction. In other words, the first stage of the chrome ore-

lime melt reduction is the second step of the ferrochromesilicon oxidation and the second stage chrome ore-lime melt reduction is the first step of the ferrochromesilicon oxidation. Therefore the first stage slag referred to herein is the slag resulting from the first stage reduction of the chrome ore-lime melt which is the second step of the ferrochromesilicon oxidation. It is one of the materials charged to the reaction vessel in the first step of the ferrochromesilicon oxidation which is also the second stage reduction of the chrome ore-lime melt. For purposes of clarity we shall refer to the first stage slag also as an intermediate slag.

The reducing agent of Step (1) (primary ferrochromesilicon) is employed in excess over that required to react with all of the oxides of the first stage or intermediate slag so that all or nearly all of the metal values of the first stage or intermediate slag, particularly chromium, are recovered. The oxidizing addition (chromium ore-lime melt) of Step (2) is employed in excess of that required to react with the secondary ferrochromesilicon (reducing agent). The resultant ferrochromium is low in carbon and silicon, and the chromium remaining in the first stage slag is recovered in Step (1) of the subsequent heat. By proper balancing of the quantities of primary ferrochromesilicon and chrome ore-lime melt employed, a consistent ferrochromium alloy is produced.

The primary ferrochromesilicon of Step (1) is commonly produced by reduction of chromite ore and silica with carbon in an electric furnace, and the molten chromium-rich slag employed in Step (2), (ore-lime melt) is commonly produced by fusing chromite ore and lime. In practice, the slags enter the reaction in the molten state while the ferrochromesilicon alloys may be added in either molten or solid form.

It will be obvious from the above that the described process produces ferrochromium alloys having chromium contents that depend entirely upon the Cr/Fe ratios of the chromite ores employed. If a chromite ore, having a Cr/Fe ratio of about 3 (three parts Cr to one part Fe) is employed, the process will consistently yield a low carbon, low silicon ferrochromium containing about 67% to 73% chromium. By employing an exceptionally high grade chromite ore having a Cr/Fe ratio in the range of 4 (four parts Cr to one part Fe), it is possible by this process to produce low carbon, low silicon ferrochromium containing from about 75% to 80% chromium. However, such high grade ores are rare and in short supply and they are not suitable for producing an alloy containing over 80% chromium.

We have discovered a new and novel method which consists of a modification of the two-step process set forth above and taught by United States Patent 1,543,321, whereby at a modest sacrifice of the chromium content of ferrochromium obtained from one or more heats, a low carbon, low silicon ferrochromium may be obtained from a selected heat of greatly increased chromium content.

Although a significant feature of our invention is the production of very high (75% or better) chromium content, low carbon and low silicon ferrochromium, our method may be successfully employed in conjunction with a chromite ore having any given chromium content or Cr/Fe ratio to upgrade the chromium content of preselected heats in a series of heats.

We have found that our method can be applied to the production of low carbon, low silicon ferrochromium without lowering the chromium content of any individual heat to below the minimum chromium content of the grade specification. For example, our method may be employed for producing low carbon and low silicon ferrochromium containing over 75% chromium and even over 80% chromium from the usual metallurgical grades of chromite ore employed to produce low carbon, low silicon ferrochromium having chromium contents within the specified range of 67% to 73% without any substantial increase in or alteration of the procedures and costs and without depleting the chromium content of preceding or subsequent heats below that which will continue to fall within the ranges of 67% to 73%.

As stated above, if reducing agents, such as silicon in the form of ferrochromesilicon, are added to molten chromite in small but increasing amounts, e.g. 10%, 20%, etc. of the stoichiometrical requirements, the Cr/Fe ratio of the ore or slag is increased by the preferential reduction of the iron content along with some of the chromium. If we start with an ore-lime melt having a Cr/Fe ratio of 3 and add 10% of the stoichiometric requirements, we may obtain a beneficiated melt with a Cr/Fe ratio of about 4. By adding 30% we attain a ratio of 7 or 8. However, when large quantities of ferrochromesilicon are added, we find that there is a reversal in the preferential reduction and the final slag does not have a high Cr/Fe ratio. As the stoichiometric quantity approaches 100%, the Cr/Fe ratio drops to about 4 or 5.

The percentage of the stoichiometric requirements where a reversal in preferential reduction occurs is not precisely known and it is undoubtedly a function of various factors, such as composition and temperature. However, we have determined from experimentation, that the reversal takes place in the range of 50% to 70% of the stoichiometric requirements. Thus, it is evident that as ferrochromesilicon is added to the molten ore and its quantity rises to 10%, 20%, 30%, etc. of the stoichiometric requirements, iron is selectively reduced, then at a quantity between 50% and 70% of the stoichiometric requirements additional ferrochromesilicon results in the preferential reduction of the chromium.

In the process of the present invention, we take advantage of the reversal of preferential reduction by reducing the quantity of primary ferrochromesilicon employed in Step (1) of the above-described two-step process to effect a small but controlled increase in the chromium content and the Cr/Fe ratio of the resultant first stage or intermediate slag (of Step (2)).

The enhanced Cr/Fe ratio of the first stage or intermediate slag experienced in the present process is significant in that it enables our process to effect particularly high chromium ferrochromium in an efficient manner which far excels the prior art practices.

In the utilization of the two step process described above and set forth in U.S. Patent 1,543,321, Danieli et al. essentially all the chromium and iron oxides in the chrome ore are reduced and essentially all the silicon in the primary ferrochromesilicon is oxidized. Consequently, the silicon content of the primary ferrochromesilicon must equal the amount required to effectively reduce all chromium and iron oxides in the ore. This effective stoichiometric amount differs from the calculated stoichiometric amount because some of the silicon may be lost as dust or may be oxidized by air or other reactants, and these losses are determined by operating factors such as temperature, size of ferrochromesilicon used, use of solid as opposed to molten ferrochromesilicon, and other variables. We have found under our particular conditions that the effective stoichiometric amount is about 1.15 times the amount calculated from the chemical reactions. If this amount is exceeded the silicon content of the secondary ferrochromesilicon will gradually build up and ultimately result in producing ferrochromium with a high silicon content. If less than the stoichiometric amount is added, the chromium content of the intermediate slag increases and ultimately the chromium content of the discard slag will also increase. In the Danieli process there is a large excess of reducing agent in Step (1) and a large excess of oxidant in Step (2). It is possible therefore to have variations in the amount of silicon (as primary ferrochromesilicon) added in several heats but this cannot be continued for a long period. The amount of primary ferrochromesilicon used is usually equal to 400 percent of the stoichiometric requirement for reducing the chrome and

iron oxides of the intermediate slag when producing the 67 percent to 73 percent chromium ferrochrome from chromite ore having a Cr/Fe ratio of about 3. However, in treating this ore under different conditions it is possible to employ as little as 150 percent or as much as 600 percent of the stoichiometric requirements to reduce the chrome and iron oxides of the intermediate slag. Because of this wide range it is possible to conduct the process with molten reactants without knowing the exact composition or even the exact weight of either.

In our modification we reduce the quantity of primary ferrochromesilicon in Step (1) of the process by an amount which we find will lower the silicon content of the secondary ferrochromesilicon an amount that will result in only a small sacrifice in the chromium content of the low carbon, low silicon ferrochromium produced in the subsequent Step (2). The amount of reduction depends, of course, on the degree of sacrifice which may be tolerated in respect to the reduction of the chromium content of the ferrochromium alloy of the individual heat. For example, we have had particular success by reducing the relative weight of primary ferrochromesilicon by about 12% while effecting the two-step process in the manufacture of 67% to 73% chromium ferrochromium from chromite ore that has a Cr/Fe ratio of 3. The primary ferrochromesilicon in this case contained about 49% silicon. The chromium content of the resultant ferrochromium dropped from 72% (the previous heat) to about 70% so as to remain in the specification limits of 67% to 73%. The Cr_2O_3 content of the first stage or intermediate slag rose from 9% to 13% without an accompanying increase in FeO.

A reduction in primary ferrochloromesilicon in Step (1) preferably should amount to at least about 5% (relative weight) to effect a measurable increase of Cr_2O_3 in the first stage slag. It would not be desirable to exceed about a 25% (relative weight) decrease for any given heat since such a reduction would produce a ferrochromium of undesirably low chromium content. Thus, it is preferable to maintain the primary ferrochromesilicon addition to relative amounts of from 75% to 95% of the normal effective stoichiometric addition weight.

Each time such relative weight reduction in primary ferrochromesilicon is made, the first stage or intermediate slag of the resultant Step (2) will exhibit a corresponding rise in Cr_2O_3 and a further improved Cr/Fe ratio. Such reduction may be practiced in one or a succession of heats depending on the level of chromium one wishes to attain in the selected heat. We have had particular success in reducing the quantity of ferrochromesilicon for two heats and taking advantage of the increased chromium and Cr/Fe ratio of the first stage or intermediate slag during the third heat.

To take advantage of the chromium build-up in the first stage or intermediate slag at the selected heat we employ a quantity of primary ferrochromesilicon substantially corresponding to the primary ferrochromesilicon normally employed during the two-stage process, plus a quantity corresponding to the reduction in primary ferrochromesilicon employed during the preceding heat or heats wherein the chromium content of the first stage slag was enhanced. Such enlarged mass of primary ferrochromesilicon is divided into relatively large and small portions, the large portion being employed as the reducing agent for the first stage or intermediate slag, and the smaller portions are added to the chrome ore-lime melt to selectively reduce the iron content. These reactions result in a high chromium content secondary ferrochromesilicon with an improved Cr/Fe ratio and a lower than normal silicon content, plus a beneficiated chrome ore-lime melt. The enriched secondary ferrochromesilicon is then added to the beneficiated chrome ore-lime melt and a low carbon, low silicon ferrochromium alloy which contains more than the normal amount of chromium is decanted and cast in the normal manner.

The quantity of primary ferrochromesilicon employed to selectively reduce the iron content of the ore-lime melt in the recovery step of the present process will vary, of course, in accordance with the size of the enlarged mass of primary ferrochromesilicon as well as its division. Such quantity may constitute as little as 10%, by weight, of the stoichiometric requirements for reducing such melt to as much as 70%, by weight, of such requirements.

During the chrome ore-lime melt beneficiation step, there is produced a somewhat low chromium ferrochromium. The heat following that in which the high chromium ferrochromium is obtained is preferably reacted in a vessel containing the molten low chromium alloy. The secondary ferrochromesilicon for this heat is obtained by reacting the first stage or intermediate slag from the high chromium heat with the normal amount of primary ferrochromesilicon. We have found that the low chromium ferrochromium alloy produced by the benefication step of our process is of such volume and chromium content that upon reaction of the heat following the beneficiation step in the presence of such low chromium ferrochromium, the final product or combined ferrochromium contains a chromium content that is substantially equivalent to that of the preceding heats.

The method of the present invention is best described by reference to the flow sheet of the accompanying drawing and an illustrative example.

In the drawings, FIGURE 1 and FIGURE 2 are a single flow sheet which illustrate the present process. FIGURE 2 is a continuation of the flow sheet of FIGURE 1. Carbon in the form of coal and coke is introduced as the reducing agent into an electric furnace **10** along with chromite ore and quartzite (a source of silicon). The chromite ore has a Cr/Fe ratio of about 3. The decanted metal consists of a primary ferrochromesilicon containing about 49% Si, 34% Cr and 16% Fe.

In accordance with standard procedure in effecting the two-step process such as is set forth in United States Patent 1,543,321, Steps (1) and (2) of a conventional heat, shown generally at A, take place in reaction vessels **14** and **16**, respectively.

A quantity of primary ferrochromesilicon alloy (5,100 lbs.) is added to the reaction vessel **14**, along with a quantity, approximately 21,500 lbs., of a first stage or intermediate slag from Step (2) of a preceding heat which assayed 9% Cr_2O_3 and 1.5% FeO. The quantity of primary ferrochromesilicon added is equal to the effective stoichiometric amount required to reduce 24,000 pounds of chrome ore-lime melt containing 27 percent Cr_2O_3 and 8 percent FeO. This quantity of primary ferrochromesilicon is also equal to approximately 400 percent of the stoichiometric amount required to effect complete reduction of the first stage or intermediate slag.

There is decanted from the reaction vessel **14** approximately 5,700 lbs. of secondary ferrochromesilicon A. This alloy contains substantially less silicon than the primary ferrochromesilicon, but sufficient to reduce the ore-lime melt to produce the ferrochromium product and a first stage or intermediate slag. The secondary ferrochromesilicon also contains substantially all of the metal values of the primary ferrochromesilicon and the first stage or intermediate slag.

A molten ore-lime melt is created by additions of chromite ore and lime to electric furnace **12**. This chromite ore is essentially the same chemically as that employed in the production of the primary ferrochromesilicon. The ore-lime melt has been determined to contain about 27% Cr_2O_3 and 8% FeO.

In Step (2) of heat A, a quantity, 24,000 lbs., of the ore-lime melt is added to the reaction vessel **16** along with the 5,700 lbs. of secondary ferrochromesilicon A from reaction vessel **14**. There is decanted from vessel **16** approximately 8,300 lbs. of a low carbon, low silicon ferrochromium A which contains 72% chromium. The slag from vessel **16** is the first stage or intermediate slag A from

heat A and weighs 21,500 lbs. This first stage or intermediate slag A is used in Step (1) of the succeeding heat B and contains equivalent chromium and iron to the employed in Step (1) of heat A (9% Cr_2O_3—1.5% FeO).

Since the first stage or intermediate slag A produced by heat A is substantially identical in weight and composition to the first sage or intermediate slag employed in Step (1) from a preceding heat, the procedure of heat A may be repeated to consistently produce low carbon, low silicon ferrochromium alloy of 72% chromium. However, in heat B we commence to deviate from this procedure to enable the production of a very high chromium heat (preselected to be heat D).

In heat B, the first stage or intermediate slag A from vessel **16** is introduced into a reaction vessel **18** along with 4,500 lbs. of the primary ferrochromesilicon. It should be noted that this addition constitutes a relative reduction of approximately 12% of primary ferrochromesilicon. The primary ferrochromesilicon of heat B is in such quantity to be approximately 369% of that required to stoichiometrically reduce the first stage or intermediate slag.

There is decanted from the reaction vessel **18**, 5,100 lbs. of secondary ferrochromesilicon B which is introduced into the reaction vessel **20** along with the normal quantity (24,000 lbs.) of ore-lime melt. This results in 7,300 lbs. of ferrochromium B which contains only 70% chromium. Such level of chromium is sufficiently high to meet the usual requirements of 67% to 73% for this grade. The first stage or intermediate slag B, however, amounts to 21,800 lbs. and contains 13% Cr_2O_3 and 1.5% FeO.

The altered first stage or intermediate slag B of heat B is introduced into reaction vessel **22** of heat C along with another reduced quantity (4,500 lbs.) of primary ferrochromesilicon alloy. This quantity of primary ferrochromesilicon now amounts to only 259% of that required to reduce the now enriched first stage or intermediate slag B. The reaction yields 5,400 lbs. of secondary ferrochromesilicon C. When this alloy is reacted with the standard 24,000 lbs. of ore-lime melt in vessel **24**, a ferrochromium (7,300 lbs.) is produced which exhibits a chromium content of 70%. It is apparent that the secondary ferrochromesilicon C of heat C is so enriched from the enriched first stage or intermediate slag from heat B, particularly insofar as the Cr/Fe ratio is concerned, that the ferrochromium of heat C exhibits a relatively high chromium content despite the fact that the reducing powers of the secondary ferrochromesilicon C are further depleted. Of particular significance is the fact that the first stage or intermediate slag C from Step (2) of heat C exhibits a still further increase in Cr_2O_3 and a further enhanced Cr/Fe ratio. This slag amounts to 22,100 lbs. and analyzes 17% Cr_2O_3 and 1.5% FeO.

The altered reactions of heats B and C may, of course, be continued to further enrich subsequent first stage or intermediate slags; however, heat D was chosen for the production of a very high chromium content ferrochromium alloy.

In heats B and C, the quantity of primary ferrochromesilicon was reduced over the normal effective stoichiometric amount (5,100 lbs.) by a total of 1,200 lbs. In heat D, therefore, approximately 6,300 lbs. of primary ferrochromesilicon are employed (the normal amount, plus 1,200 lbs.). Of this, 4,600 lbs. are introduced into the reaction vessel **26**, along with the first stage or intermediate slag C from heat C. After the primary ferrochromesilicon reacts with the first stage or intermediate slag, the secondary ferrochromesilicon is allowed to remain in the ladle. Ore-lime melt (24,000 lbs.) is beneficiated in another vessel **28** by the addition of the remaining portion of primary ferrochromesilicon (1,700 lbs.). The beneficiated ore-lime melt is then decanted into reaction vessel **30**. Subsequently, the secondary ferrochromesilicon is decanted from reaction vessel **26** into reaction vessel **30**. There is decanted from the reaction vessel **30**, 7,100 lbs. of a low carbon, low silicon, high chromium ferrochromium D containing approximately 81.7% chromium.

Vessel **28** contains 3,000 lbs. of a relatively low chromium (low C, low Si) ferrochromium alloy (50% Cr) which may be cast and sold. In this case, the first stage or intermediate slag D obtained from reaction vessel **30**, is equivalent in weight and analysis to the first stage or intermediate slag A of heat A (21,500 lbs. 9% Cr_2O_3 and 1.5% FeO), and may be employed to produce a 72% chromium ferrochromium in the normal fashion or the quantity of primary ferrochromesilicon may be lowered (preferably by 5% to 25%, by weight, of its normal concentration) to enrich a first stage or intermediate slag in the manner of heats B and C so that the process of the present invention is repeated.

If the 50% chromium ferrochromium alloy is not regarded as being marketable, it is conveyed into a reaction vessel **34**. The first stage or intermediate slag D from reaction vessel **30** is conveyed into a reaction vessel **32** along with the normal quantity of primary ferrochromesilicon alloy (5,100 lbs.) The secondary ferrochromesilicon alloy E from this reaction (5,700 lbs.) is conveyed into the reaction vessel **34** along with a normal charge of ore-lime melt (24,000 lbs.). Since the quantity of low chromium ferrochromium is not large (3,000 lbs.) and the chromium content constitutes half of its analysis (50%), the low carbon, low silicon ferrochromium E, decanted from vessel **34**, contains 69% chromium, which is well within the marketable range of 67% to 73%. The first stage or intermediate slag E from heat E is equivalent to the first stage or intermediate slag A of heat A (21,500 lbs., 9% Cr_2O_3—1.5% FeO) so that heat F (not shown) may be employed as a regular Step (1) as in heat A, or to enrich the first stage or intermediate slag, as in heats B and C.

It is to be noted that in each heat, sufficient primary ferrochromesilicon alloy is employed to remove substantially all of the metal values from the first stage or intermediate slags and that the discard slags from all of these reactions contain only about 1% Cr_2O_3.

The exact quantities of primary ferrochromesilicon employed are, of course, dependent on many variables. For example, under the conditions of our reaction as shown by heat A where chromite ore of Cr/Fe ratio of 3 is employed to obtain 67% to 73% Cr ferrochromium, using the volume of materials shown at reaction temperatures of about 3200° F., we find that the silicon content of the primary ferrochromesilicon should amount to about 400% of the stoichiometric requirements; however, when reacting different chromium containing ores in different volumes and at different temperatures, a greater or lesser excess may be required. In each instance, however, it is preferable to lower the primary ferrochromesilicon from 5% to 25% of its own weight since such reduction will enrich the first stage or intermediate slag regardless of the exact materials employed and the conditions of the reaction.

The flow sheet of the drawing and the example shown and described are illustrative only. It is obvious that the method of the present invention may be employed to increase the chromium content of any such two-step process, regardless of the level of chromium normally obtained, and the upgrading step, such as shown by heat D, may be effected after one or any number of first stage slag enrichment steps, such as are illustrated by heats B and C of the flow sheet, so that any specifically desired high chromium level may be attained from a preselected heat.

Also, upgrading of the depleted chromium ferrochromium, such as shown for heat E, is relative so that such recovery may be effected regardless of the normal chromium level ferrochromium being produced by the two-step process.

It will be understood that the terms "primary" and "secondary" as applied to the ferrochromesilicon alloys are relative terms and are not intended to identify a specific silicon content. The primary ferrochromesilicon alloy made up in furnace **10** contains 49% Si; however, such silicon content may vary widely without departing from the scope of the present process since this alloy will be utilized in accordance with its reducing powers. Generally, the secondary ferrochromesilicon will contain less silicon than the primary ferrochromesilicon; however, the silicon content of this alloy may also vary widely in accordance with the exact reaction taking place.

Chromite ores consist mineralogically of the spinel group and contain primarily chromite ($FeO \cdot Cr_2O_3$) and magnesiochromite ($MgO \cdot Cr_2O_3$). In either of these, Cr_2O_3 may be partially replaced by Al_2O_3. Most chromite ores thus contain significant quantities of magnesia and alumina, e.g., 10% to 18% MgO and 8% to 12% Al_2O_3, but these oxides are not reduced, but rather form a slag. The ores may also contain minor or trace amounts of reducible oxides such as nickel and manganese which enter the ferrochromium. It will be understood that the two-stage process for producing low carbon, low silicon ferrochromium described above and the method of the present invention is applicable to all such ores though they may vary in origin and content.

In the illustrative flow sheet of the drawing, a total of eleven reaction vessels are depicted (**14** through **34**). Such numerous vessels are illustrated for convenience of description only since, normally, vessel **14** will be the same ladle as vessels **18**, **22**, etc. Extra equipment is not required in carrying out the method of the present invention.

Also, in the above description, reference is made to decanting ferrochromesilicon alloy from various of the reaction vessels. It is our practice to use the secondary ferrochromesilicon alloy in the molten state although, as previously stated, it may be cast and crushed for use in the solid state. The molten ferrochromesilicon in the reaction vessel is covered by a thick layer of slag and it is separated from the slag by using a specially designed vessel which, when tilted, permits the molten ferrochromesilicon alloy to come out first. It will be understood that any of the commercially accepted methods and devices for removing the molten alloy from its slag cover may be employed in conjunction with the present method.

Also, the reaction vessels themselves may be any of the well-known refractory lined vessels employed to contain molten reactive materials. A common vessel for this use is a refractory (magnesia) lined ladle. The electric furnaces employed may be any of the well-known commercially available electric reduction furnaces employed for these purposes.

The invention is not limited to the preferred embodiments of the flow sheet or examples, but may be otherwise embodied or practiced within the scope of the following claims.

We claim:

1. In a continuous two-step process for reducing chromite ore to obtain a low silicon ferrochromium wherein in Step 1 silicon is the form of a primary ferrochromesilicon alloy is reacted with a molten intermediate slag from Step 2 of a preceding heat to form a secondary ferrochromesilicon alloy and a discard slag and in Step 2 the secondary ferrochromesilicon alloy is reacted with a chromite ore-lime melt to produce the low silicon ferrochromium and reproduce the intermediate slag, the amount of primary ferrochromesilicon being substantially equal to the effective stoichiometric quantity required to reduce the chromium and iron oxides in the chrome ore-lime melt, the improvement which consists of:

(A) adding less than the effective stoichiometric quantity of primary ferrochromesilicon to at least one heat to enrich the chromium content of the intermediate slag and

(B) in a subsequent heat,

(1) adding more than the effective stoichiometric quantity of primary ferrochromesilicon, a portion thereof being added to a chrome ore-lime melt to beneficiate the ore-lime melt and a portion being added to the intermediate slag to produce a chromium enriched secondary ferrochromesilicon, the total excess primary ferrochromesilicon being substantially equal to the deficiency of primary ferrochromesilicon in the preceding heats and

(2) reacting the beneficiated chrome ore-lime melt with the chromium enriched secondary ferrochromesilicon to produce a high chromium, low silicon ferrochromium alloy and reproduce the intermediate slag.

2. The process as set forth in claim **1** wherein the primary ferrochromesilicon alloy in paragraph A is 75 percent to 95 percent of the effective stoichiometric quantity.

3. In a continuous two-step process for reducing chromite ore to obtain a low silicon ferrochromium wherein in Step 1 silicon in the form of a primary ferrochromesilicon alloy is reacted with a molten intermediate slag from Step 2 of a preceding heat to form a secondary ferrochromesilicon alloy and a discard slag and in Step 2 the secondary ferrochromesilicon alloy is reacted with a chromite ore-lime melt to produce the low silicon ferrochromium and reproduce the intermediate slag, the amount of primary ferrochromesilicon being substantially equal to the effective stoichiometric quantity required to reduce the chromium and iron oxides in the chrome ore-lime melt, the improvement which consists of:

(A) adding less than the effective stoichiometric quantity of primary ferrochromesilicon to at least one heat to enrich the chromium content of the intermediate slag and

(B) in a subsequent heat,

(1) reacting a chrome ore-lime melt with a reducing agent to beneficiate the ore-lime melt

(2) reacting a primary ferrochromesilicon with the intermediate slag from the preceding heat to produce a chromium enriched secondary ferrochromesilicon, the total amount of primary ferrochromesilicon and reducing agent utilized in B(1) and B(2) being substantially equal to the effective stoichiometric quantity required to reduce all oxide values in the chrome ore-lime melt plus the deficiency of primary ferrochromesilicon in the preceding heats and

(3) reacting the beneficiated chrome ore-lime melt of step B(1) with the chromium enriched secondary ferrochromesilicon of step B(2) to produce a high chromium, low silicon ferrochrome alloy and reproduce the intermediate slag.

4. The process as set forth in claim **3** wherein the primary ferrochromesilicon alloy in paragraph A is 75 percent to 95 percent of the effective stoichiometric quantity.

5. In a continuous two-step process for reducing chromite to obtain a low silicon ferrochromium wherein in Step 1 silicon in the form of a primary ferrochromesilicon alloy is reacted with a molten intermediate slag from Step 2 of a preceding heat to form a secondary ferrochromesilicon alloy and a discard slag and in Step 2 the secondary ferrochromesilicon alloy is reacted with a chromite ore-lime melt to produce the low silicon ferrochromium and reproduce the intermediate slag, the amount of primary ferrochromesilicon being substantially equal to the effective stoichiometric quantity required to reduce the chromium and iron oxides in the chrome ore-lime melt, the improvement which consists of:

(A) adding less than the effective stoichiometric quantity of primary ferrochromesilicon to at least one heat to enrich the chromium content of the intermediate slag and

(B) in a subsequent heat,

(1) reacting a chrome ore-lime melt with primary ferrochromesilicon in amounts of from about 10 percent to 70 percent by weight of the stoichiometric requirements for reducing the melt to beneficiate the chrome ore-lime melt

(2) reacting primary ferrochromesilicon with the intermediate slag from the preceding heat to produce a chromium enriched secondary ferrochromesilicon, the total primary ferrochromesilicon used in Step B(1) and Step B(2) being substantially equal to the effective stoichiometric quantity plus the deficiency of primary ferrochromesilicon utilized in paragraph A and

(3) reacting the beneficiated chrome ore-lime melt of Step B(1) with the chromium enriched secondary ferrochromesilicon of Step B(2) to produce a high chromium, low silicon ferrochrome alloy and reproduce the intermediate slag.

6. The process as set forth in claim 5 wherein the primary ferrochromesilicon alloy in paragraph A is 75 percent to 95 percent of the effective stoichiometric quantity.

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