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PROCESS FOR THE PRODUCTION OF LOW SULFUR FERROCHROMIUM

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The present invention relates to a process for producing ferrochromium alloys. More particularly, the present invention relates to a process for producing ferrochromium alloys having very low sulfur contents.

Certain elements are known to cause highly undesirable effects when present as constituents in structural metals. Among these elements, sulfur is one of the most detrimental due to its adverse effects on the high-temperature properties of the metal.

Since a major use of ferroalloys is in the manufacture of structural metals and other materials in which the presence of sulfur is deleterious, the elimination of sulfur from ferroalloys has been a continuing and long standing problem in the metallurgical art. However, in spite of considerable effort and study, up to the present time, insofar as can be determined, a simple and direct process for producing low sulfur ferrochromium has not been found.

It is therefore an object of the present invention to provide a direct, simple and economical process for the production of ferrochromium alloys having a very low sulfur content.

Other objects will be apparent from the following description and claims.

A process in accordance with the present invention for producing low sulfur ferrochromium comprises preparing ferrochromium metal substantially in the form of

$$(Fe,Cr)_7C_3$$

together with a fluid slag by smelting a mixture of chrome ore, carbon and slag-forming material in which mixture the molar base to acid ratio of the slag-forming material is between about 2.5:1 and about 8.5:1, preferably between 3.5:1 and 6:1, and in which the molar ratio of lime to silica is greater than about 0.75.

Ferrochromium alloy which is produced from the usual source materials in accordance with the present invention has a sulfur content of less than about 0.015 percent, a silicon content of less than about 2 percent, and a phosphorous content of less than about 0.02 percent. As a consequence, this material is of high industrial utility.

The compositional ranges in weight percent of ferrochromium alloys which can be readily produced in accordance with the present invention from the usual commercial starting materials are set forth in Table I.

TABLE I

	Percent
Cr	50 to 73
C	8 to 10
Si	0.1 to 2.0
S	0.003 to 0.015
N	maximum 0.015

Balance, iron and incidental impurities.

For purposes of the present invention, the oxygen-containing calcium and magnesium materials in the smelting mixture are considered to be in the form of CaO and

MgO, respectively, and the aforementioned molar base to acid ratio of the slag forming material is calculated as follows:

$$\text{Molar B/A} = \frac{\text{moles of CaO} + \text{moles of MgO}}{\text{moles of SiO}_2}$$

Alumina and other oxides present in the smelting mixture are not included in the computation of the base to acid ratio.

In the practice of the present invention, a mixture of chrome ore, carbon, and slag-forming material is smelted in an electric furnace to provide molten ferro-chromium metal substantially in the form of $(Fe,Cr)_7C_3$ together with a fluid, highly basic slag from which the metal is ultimately separated and solidified. In general, all known commercially available chrome ores can be used in the present process and the carbon material in the furnace charge can be in any convenient form such as coal, coke, and the like. The charge can contain the usual amount of sulfur impurities which is generally between about 0.1 and 0.3 percent by weight. Substantially greater amounts of sulfur can be present in the charge and the alloy produced by the present invention will nevertheless have a surprisingly low sulfur content. The chrome ore can be in the form of lumps or fines and the fines can be briquetted or not as desired. If fines are used and formed into briquets together with reductant and slag-forming material, a considerable saving in power consumption is realized.

In preparing the furnace charge, it is essential that the base to acid ratio of the slag-forming material be in the range of 2.5:1 and 8.5:1, preferably between 3.5:1 and 6:1, in order to ultimately provide a ferrochromium alloy with less than 0.015 percent sulfur. It is also necessary that the molar ratio of lime to silica in the charge be greater than about 0.75 to ensure a silicon content of less than 2 percent and to avoid an increase in sulfur content to above 0.015 percent. If the lime to silica ratio is less than about 0.75, silica becomes available for reduction which results in an increase in the silicon level of the alloy. At the same time, under these circumstances, the carbon content of the alloy decreases and the sulfur content increases.

Since the available ores do not generally provide the molar ratios required by the present invention, additional materials such as burned lime, limestone, dolomite, quartz and the like are added to the furnace charge for this purpose.

A further requirement of the present invention is that the slag produced in the smelting of the furnace charge be high melting and highly fluid in the molten state in order to be effective in the process and to permit convenient separation of the metal product. In this respect slags having a 25 poise temperature of at least 1575° C. are required in the present process.

In order to provide a slag having the necessary melting point and fluidity characteristics, alumina can be added to the furnace charge in the amount required. This alumina addition, of course, does not affect the base to acid ratio of the charge.

The compositional ranges set forth in Table II are specific proportions of slag-forming materials which satisfy the present invention.

Table III sets forth ranges for slag-forming material which can be used in the present invention providing the aforedescribed molar ratios are satisfied. In the tables and elsewhere in this description, only CaO, MgO,

Al_2O_3 and SiO_2 are considered as constituents of slag-forming material; chrome and iron oxides and contaminants derived from the ore and reductant are disregarded.

TABLE II

Total Slag-Forming Material weight percent		25 Poise Temperature, ° C.
	Percent	
SiO_2	20	1,649
CaO	20	
MgO	30	
Al_2O_3	30	
	100	
Sio	20	1,583
CaO	25	
MgO	30	
Al_2O_3	25	
	100	

TABLE III.—COMPOSITION RANGE—TOTAL SLAG-FORMING MATERIAL WEIGHT PERCENT

CaO	13 to 35
MgO	22 to 35
Al_2O_3	25 to 42
SiO_2	9 to 28

In the process of the present invention, the carbon stoichiometry is of importance and must be adjusted so that the final ferrochromium alloy is substantially, i.e. 95 percent or more, in the form of $(Fe,Cr)_7C_3$. Accordingly, the preferred carbon content of the molten alloy prepared by smelting the furnace charge is 8 to 9 percent, although carbon contents up to 10 percent provide highly satisfactory ferrochromium alloys having sulfur contents below 0.015 percent and silicon contents below 2.0 percent.

Carbon contents in the molten alloy which are higher than 10 percent are undesirable since they tend to cause the formation of substantial amounts of the Cr_3C_2 type of carbide which is highly refractory and interferes with recovery of the alloy. Moreover, the amount of carbon required in the furnace charge to produce the higher carbon levels tends to cause an increase of silicon in the alloy.

It has been found that molten ferrochromium, prepared in the process of this invention and containing between 8.5 and 10 percent carbon, tends to reject (as graphite) practically all of the carbon in excess of that required to form $(Fe,Cr)_7C_3$ when cooled at a rate of about 150° C. to 300° C. per hour.

As mentioned hereinabove, the silicon content of the ferrochromium alloy product of this invention is limited to less than about 2 percent by adjusting the lime to silica ratio in the furnace charge to 0.75 or more. Additionally, the silicon content of the alloy can be adjusted to particular values less than about 2.0 percent by controlling the carbon stoichiometry and/or the sizing of the furnace charge constituents. For example, carbon in the charge, in excess of the stoichiometric amount required to form $(Fe,Cr)_7C_3$ by reduction of the ore, tends to cause an increase in the silicon content of the alloy. Also, decreasing the particle size of the furnace charge tends to increase the silicon content.

In the present invention, by adjusting the particle size of the furnace charge and by varying the carbon content within the limits which will result in a substantially $(Fe,Cr)_7C_3$ material, the silicon content of the alloy can be controlled in the range from about 0.1 to about 2.0 percent.

Control of the silicon content of the ferrochromium alloy is important in that silicon affects the solidity and the friability of the metal. Very low-silicon metal can be made by the present process, however if the silicon content is less than about 0.15 percent, the metal is "gassy" and full of small voids. A silicon content in the range of 0.5 to 2.0 percent will result in a dense, solid but still friable alloy. If the metal is to be used as an addition agent to a steel bath, it will be generally preferable to maintain the silicon content in the 0.5 to 2.0 percent range. When the metal is to be further processed as by a solid state decarburizing process, the solidity and denseness of the metal are unimportant, and the silicon may be less than 0.5 percent if desired. A low-silicon content is advantageous when the molten metal is to be decarburized by oxygen blowing since this reduces slag formation resulting from oxidation of silicon and therefore refractory attack.

The following examples are provided to further illustrate the present invention.

Example I

The following mix was prepared as a furnace charge.

	Lbs.
Dyke flotation concentrate 32 by 200 mesh	600
Poco coal 1 inch by D mesh	176
Wood chips	50
Lime 2 inches by D mesh	60

ANALYSIS OF MIX MATERIALS

	DFC Ore, percent	Lime, percent	Poco Coal, percent	Wood Chips, percent
Cr_2O_3	54.8			
FeO	19.5			
CaO, MgO	8.4	96.9		
Al_2O_3	12.4			
SiO_2	2.9			
Fixed Carbon			72.67	25.5
Volatiles			23.80	70.4
Ash			3.53	4.0

The mix had a molar base to acid ratio of 5.93 and was calculated to produce the following products:

	Percent
Alloy:	
Cr	61.0
Fe	28.69
C	9.20
Si	0.1
S	<0.01
Impurities	1.0
Slag:	
CaO	24.19
MgO	25.72
Al_2O_3	39.25
SiO_2	10.84

The calculated slag composition is not adjusted for subsequently dissolved Cr_2O_3 or volatilization and dusting losses.

The mix was fed to an electric furnace having an oval hearth in which power was supplied by two 17-inch diameter electrodes. The furnace lining was rammed carbon paste with chrome ore refractory backup. The furnace was operated at about 1000 kilowatts at 60 to 90 volts. The average composition of metal tapped from the furnace was as follows:

	Percent
Cr	61.01
Fe	28.31
C	9.54
Si	0.13
S	0.009
Impurities	1.0

The metal was gassy, i.e. contained numerous voids but was free of gross slag inclusions.

The chilled slag recovered from the casting mold analyzed:

	Percent
CaO	20.41
MgO	20.79
Al_2O_3	28.40
SiO_2	11.14
A.I. Cr [1]	3.73
S	0.30
Metallics	7.47

[1] Chromium as acid-insoluble Cr_2O_3.

In the above-described operation the furnace operated without difficulty and required only normal stoking. There were no troublesome "blows" and dusting was minimal.

Overall recovery of chromium was 96 percent.

Example II

The following mix was prepared as a furnace charge.

	Lbs.
Dyke flotation concentrate 32 by 200 mesh	100
Poco coal 90%, −325 mesh	31
Lime hydrate 200 by D mesh	17½
Coal tar	4½
Pitch	4½

ANALYSIS OF MIX MATERIALS

	DFC Ore, percent	Lime Hydrate, percent	Poco Coal, percent	Tar	Pitch
Cr_2O_3	54.8			Sp. Gr. 1.176	M.P. 125° F.
Fe_2O_3	19.5				
CaO } MgO	8.40	67.5		Sp. Visc. at 50 °C.	
Al_2O_3	12.40			24.3	
SiO_2	2.90				
Fixed Carbon			72.67		
Volatiles			23.80		
Ash			3.53		

This mix had a molar base to acid ratio of 6.92 and was calculated to produce the following products:

	Percent
Alloy:	
Cr	61.0
Fe	28.89
C	9.00
Si	0.1
S	<0.01
Impurities	1.0
Slag:	
CaO	32.61
MgO	22.89
Al_2O_3	35.08
SiO_2	9.89

The mix constituents were thoroughly mixed at a temperature sufficient to fluidize the binder and pressed into pillow-shaped briquets approximately 2¾ by 2 inches.

The same furnace and operating conditions were employed as in Example I.

The average composition of the metal produced was:

	Percent
Cr	61.45
Fe	27.66
C	9.56
Si	0.32
S	0.012
Impurities	1.0

The metal was solid and free of voids.

The slag recovered from the casting mold analyzed:

	Percent
CaO	21.44
MgO	16.80
Al_2O_3	28.05
SiO_2	21.16
A.I. Cr	0.53
S	0.46
Metallics	5.35

The overall recovery of chromium was 95 percent.

The form of the compacts or agglomerates used in the above process is not critical. Disc rolled pellets of ⅜- to ⅝-inch diameter and flakes ⅛ to ¼ inch thick by about 1 to 2 inches in the other two dimensions, have also been successfully used in the same manner.

Example III

The following mix was prepared as a furnace charge.

	Lbs.
SA Ore, 6 inches by D mesh	480
Transvaal Ore, 1 inch by D mesh	120
Poco coal, 1¼ inches by ¾ inch	30
Coke, ¾ inch by ½ inch	93–103
Wood chips	60
Limestone, 2 inches by D mesh	119
Quartzite, 2 inches by D mesh	14–20

ANALYSIS OF MATERIALS

	Ore		Limestone, percent	Coal, percent	Coke, percent	Wood Chips, percent	Quartzite, percent
	SA, percent	Transvaal, percent					
Cr_2O_3	43.77	44.15					
FeO	13.04	23.92					
CaO	1.56	0.61	54.5				
MgO	16.89	10.94					
Al_2O_3	12.69	14.35					
SiO_2	7.75	3.57					99.0
Fixed Carbon				71.65	88.62	25.5	
Volatiles				23.92	1.65	70.4	
Ash				4.43	9.73	4.0	

The mix had a molar base to acid ratio of 3.54 and was calculated to produce the following products:

	Percent
Alloy:	
Cr	64.50
Fe	26.4
C	9.00
Si	0.10
Slag:	
CaO	23.0
MgO	31.0
Al_2O_3	26.0
SiO_2	20.0

The mix was fed to the furnace described in Example I using an average power input of about 1000 kilowatts at 50 to 60 volts.

The average composition of the metal and slag produced is as follows:

	Percent
Alloy:	
Cr	63.09
N	0.003
C	8.9
Si	0.83
S	0.003
Fe+impurities	Balance

Slag:

CaO	23.98
MgO	24.94
Al_2O_3	23.22
SiO_2	19.48
A.I. Cr	1.32
S	0.28
Cr. (total)	3.45

Overall recovery of chromium was 94%.

In addition to the previously mentioned advantages, the slags derived from the practice of the present invention generally contain less than 4 percent Cr_2O_3 and frequently contain less than 1 percent Cr_2O_3. Since the slags of conventional smelting processes usually contain from 5 to 8 percent Cr_2O_3 it can be seen that the present invention provides a substantial increase in chromium recovery.

Another factor of importance to the economics of the process is the saving in power that may be achieved with the use of fined ores, either compacted or fed to the furnace as loose powder. With the use of fine ores, savings up to 20 percent have been realized over conventional smelting practice.

Further, the slag to alloy ratios obtained in the practice of the present invention range from 0.8 to 1.0 (fine ore practice) to 1.5 (lump ore practice) with the average being about 1.1 to 1.25. These ratios indicate a considerably higher metal recovery in the practice of the present invention than that obtained in previously known processes.

In the foregoing description the mesh sizes refer to the Tyler Series.

What is claimed is:

1. In a process for producing ferrochromium alloy by smelting a mixture of chrome ore, carbon and slag-forming material to cause reduction of the ore and the production of ferrochromium and a basic slag, the improvement for producing a low sulfur, low silicon alloy which comprises adjusting the composition of the mixture so that (1) the base to acid molar ratio of the mixture is between about 2.5:1 and 8.5:1, (2) the CaO to SiO_2 ratio of the mixture is greater than about 0.75, (3) the resulting slag has a 25 poise temperature of at least about 1575° C., and (4) the alloy produced is at least 95 percent in the form of $(Fe,Cr)_7C_3$.

2. A process in accordance with claim **1** wherein the slag forming material in the mixture is within the compositional range of 13 to 35 percent CaO, 22 to 35 percent MgO, 25 to 42 percent Al_2O_3, 9 to 28 percent SiO_2.

3. A process in accordance with claim **1** wherein the molar base to acid ratio is between 3.5:1 and 6:1.

4. In a process for producing ferrochromium alloy by smelting a charge consisting essentially of chrome ore, carbon and at least one slag-forming material selected from the group consisting of CaO, SiO_2, MgO and Al_2O_3 to cause reduction of the ore and the production of ferrochromium and a basic slag, the improvement for producing a low sulfur, low silicon high carbon alloy which comprises adjusting said charge to provide a base to acid molar ratio therein of between about 2.5:1 and 8.5:1 and a CaO to SiO_2 ratio therein of greater than about 0.75 and to provide upon reduction of the chrome ore in said charge (1) a slag having a 25 poise temperature of at least 1575° C. and (2) a ferrochromium alloy which is at least 95% in the form of $(Fe,Cr)_7C_3$, said alloy being characterized by having a sulfur content of less than 0.015 percent and a silicon content of less than 2 percent.

5. A process in accordance with claim **4** wherein said base to acid molar ratio is between 3.5:1 and 6:1.

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