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MAKING ALLOYS CONTAINING IRON, CHROMIUM, SILICON, AND CARBON FROM CHROMITE ORES

Marvin J. Udy, Niagara Falls, N. Y.

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3 Claims. (Cl. 75—11)

This invention or discovery relates to making alloys containing iron, chromium, silicon and carbon from chromite ores; and it comprises a method of improving the yield of chromium in reducing chrome iron ore and of controlling the carbon content of the reduced metal wherein the ore, which itself may advantageously be high in iron or mixed with iron ore, is smelted in a continuously operated submerged arc electric furnace together with additions of lime, silica and carbon in the relative quantities required to form with the gangue of the ore a slag containing lime plus magnesia equivalent to lime in a ratio to silica of about 1.7 to 2.2 parts by weight of lime, CaO, to one part silica, SiO_2, and to provide a considerable excess of silica over said ratio with sufficient carbon to reduce substantially all the chromium and iron of the ore to metal and also the excess silica to silicon, the smelting temperature being allowed to rise to the point of free running liquidity of the relatively basic slag, and molten slag of the stated composition and molten ferrochrome silicon metal of controlled carbon content are withdrawn from the furnace; all as more fully hereinafter set forth and as claimed.

One of the important uses for the element chromium is as an alloying constituent of various metals. In particular, chromium alloyed with iron in various ways gives non-corrodible or oxidation-resistant metals and the use of chromium for this purpose has increased greatly in recent years.

Ferrochromium made by reduction of chromite ores has been practically the only source material for making the iron-chromium corrosion-resistant alloys. In these alloys it is nearly always essential that the carbon be kept quite low and the carbon content of ferrochromium presents one of the main problems of chromium metallurgy. The cost of low carbon ferrochromium is generally double or more the cost of the high carbon grades; in fact, the cost is to some extent inversely proportional to the carbon content. Control of the carbon content in making ferrochromium is a matter of prime importance.

Generally, ferrochromium used as a source material in making chromium iron alloys low in carbon is one of the standard grades of 68 to 72 per cent, the chromium content varying according to the carbon content, and containing about 28 per cent iron, the weight ratio of chromium to iron being between 2.3 and 2.5 chromium to one of iron; while the finished commercial alloys in most cases carry 80 per cent or more iron; a weight ratio of at least 5:1 iron and chromium. To obtain the standard high grade ferrochromium, it has been considered necessary to import from distant foreign countries rich chromite ores having sufficiently high chromium-iron ratios to give on reduction the high chromium-low iron ferrochromium required. Chrome steel and iron alloys contain in most cases less than 20 per cent chromium and seldom more than 30 per cent chromium. Thus, in order to get a low carbon finished commercial alloy, it has been common practice to add a 70 per cent ferrochromium to a steel bath and therefore in effect to dilute a 70 per cent chromium metal with iron to less than half this chromium content; the necessity of removing carbon from the alloy being minimized by use of the small amount of carboniferous ferrochromium necessary to supply chromium. This has been considered economical as compared to using expensive low carbon grades of ferrochromium.

In a prior Patent No. 2,109,122, I have described and claimed a method of operating an electric furnace for production of standard ferrochromium from the higher grade ores comprising limitation of the carbon content of the metal product by maintaining a base-acid slag ratio of at least two mols lime and magnesia together to one of silica and alumina and a furnace temperature high enough to make this basic slag free running. In that method the control of the carbon content made possible by the stated adjustment of the slag ratio is associated with regularizing the furnace operation with the result that both the chromium and the iron oxides of chromite ore are reduced in a good yield and carbon in the furnace charge over that used in the reduction goes into the metal. The slag ratio of base to acid is found to be a critical factor in regularizing the furnace action for production of a standard ferrochromium containing nearly all the chromium and the iron of the chromite ore charged into the furnace. The ferrochromium produced may be any of the standard grades containing carbon from 2 per cent upward. Controlling the slag basicity in making ferrochromium gives control of the carbon content.

I have now discovered that the carbon content of ferrochromium reduced from chromite ores of all grades can be further limited, controlled and regularized by simultaneously reducing silica and maintaining the basic slag. This results in a replacement of carbon in the metal by silicon, thus lowering the carbon content. The charge in the

furnace includes with the ore regulated amounts of a carbon reducing agent, lime or limestone and silica or a siliciferous ore, the quantity of silica being more than corresponds to the lime in a 2:1 lime-silica molecular ratio. In so doing, a molten slag is made having a ratio of lime to silica between 1.7 and 2.2 by weight, which approximates the molecular ratio of $2CaO:1SiO_2$ (1.86:1 by weight) and the remainder of the silica or excess over that required for the stated slag ratio is reduced by carbon present and furnishes silicon to the metal, sufficient carbon being provided for this purpose. As the silicon in the metal increases, there is a lessening of the carbon content, the carbon in the charge being oxidized in the reduction of silica. As I have now found, in fixing the base-acid ratio in the slag, the magnesia in the ore gangue acts as a base with the added lime, and the alumina of the ore gangue remains neutral and may be disregarded. Apparently, silicate slag approaching the dibasic ratio dissolves alumina and the alumina of the ore gangue need not be taken into consideration in calculating the amount of lime required. A ratio of lime and magnesia together to silica equivalent to from 1.7 to 2.2 parts by weight of lime to 1 part silica tends to be maintained in the slag by reduction of excess silica in the furnace charge over that required for the slag ratio. The reduction of excess silica to silicon effects a high yield of ferrochromium metal from the ore with a lowering of the carbon content in the metal. The charge carries excess carbon over and above that required to reduce the chromium and the iron of the ore. As I have discovered in smelting chrome iron ores with lime and carbon in continuous operation in a submerged arc furnace with production of a slag having the stated ratio of lime to silica and at high temperatures, sufficient to keep this relatively basic silicate slag freely liquid, an excess of silica over that required for the slag ratio is reduced. A high yield of metal containing silicon and of controlled carbon content is obtained. Addition of lime accompanied by adjustment of the slag ratio with excess silica added over that required for the ratio and with excess carbon to reduce silicon gives smooth and regular furnace operation with substantially complete control of the yield and composition of the metal. Alloys composed of iron, chromium, silicon and carbon in almost any desired ratio can be made. The alloy composition can be adjusted in accordance with that desired in making any particular finished commercial chromium alloy for which the siliconized ferrochromium is to be used as an intermediate source material supplying chromium.

In continuous operation of a submerged arc furnace charged with chromite ore, carbon, lime and silica and producing molten ferrochrome silicon metal and a molten free running slag, the smelting temperature in the furnace rises with increase of slag basicity; automatically going to the melting temperature of the slag. Accordingly, the temperature in the furnace is regulated by the slag basicity and indirectly by reduction of excess silica which adjusts the slag basicity in continuous operation, that is, in non-batch operation with charging and tapping which may be intermittent.

In producing the stated intermediate iron-chromium-silicon alloy with controlled carbon content in a submerged arc furnace, I have found that, once established, the slag bath composition with silica, lime and magnesia in the approximate 1:1 oxygen ratio and the furnace temperature being about 1600–1700° C., there is tendency for an automatic maintenance of this slag composition and temperature with smooth and regular furnace operation. This is the temperature necessary to make this type of slag a free running liquid. An excess of silica over the stated ratio is reduced, and silicon enters the metal. The carbon content of the metal is lowered in proportion. The submerged arc, the approximately dibasic silicate slag and the relatively high temperature are, as I have found, critical factors making possible substantially complete control of the yield and of the silicon and carbon contents of the reduced molten metal by this expedient of adding excess silica. The excess silica, being reduced to silicon does not disturb but adjusts the balance of the slag. Excess of lime or similar base over this ratio raises the temperature of the furnace and lime is volatilized. In either event the slag ratio tends to maintain itself. There is a constant high yield of relatively low carbon metal containing silicon. The liquid slag and molten metal are tapped from the furnace by well known means. The metal may be run into molds to solidify in ingot form or into another furnace for refining to a finished chromium alloy.

In calculating the amount of lime required with the chromite ore, it is found that best results are obtained by adding an amount of CaO, allowing for the CaO in the ore, approximately equivalent to the FeO of the ore or equal to the weight of iron.

As stated, control of the carbon content in the intermediate ferrochromium alloy is secured by addition to the furnace charge of silica in excess of that going into the slag in maintaining the desired lime-silica ratio. As an effect, excess carbon reduces excess silica, giving silicon aiding in reduction of the ore and contributing to the high yield of chromium in the metal. Excess reducing agent appears in the metal as silicon. It is found that by increasing the silica and the carbon in the furnace charge the silicon content of the metal rises and the carbon content is lowered. Substantially complete reduction of chromium and iron is effected by an excess of silica and carbon, giving a metal containing usually more silicon than carbon.

In general, the carbon content of ferrochrome metal made by reducing chromium ores with carbon increases with the chromium content of the metal which in turn depends upon the ratio of chromium to iron in the ore. I find it advantageous in this connection to reduce low grade chromite ores, that is, those having a chromium iron ratio less than 2:1. Total reduction of these ores with carbon gives a metal too high in carbon to be salable. In the present invention I produce a metal carrying less carbon. Such low grade ores have heretofore been considered unavailable for making ferrochromium. The lower the chromium content of the reduced metal the lower is the carbon content in producing it in the present way. For example, it has been found advantageous in smelting a low grade chromite ore having a chromium to iron ratio less than 1 to add sufficient excess silica and carbon to the furnace charge to produce ferrochrome silicon metal containing up to 10 per cent silicon with a carbon content of 4 to 6 per cent. Such a metal can be produced as described in high yield from the ore and has been found useful for "blocking the heat" in open hearth steel manufacture after

the carbon refining by iron oxide; adding chromium and iron to the steel bath without undue addition of silicon, the silicon in a ratio of about one-sixth to one-quarter of the chromium content in the added metal serving to protect the chromium against oxidation thereof by the slag bath.

In general, by operation of the process as described, a chromite ore of any grade (or a chromiferous slag) can be reduced by carbon to produce a ferrochromium metal of any desired silicon content and a controlled carbon content. Utilizing low grade chromite ores of a chromium to iron ratio less than 2, a metal can be made containing from 2 to 50 per cent silicon with carbon running from 6 per cent down to about 0.05 per cent, according to the silicon content. Standard high grade ore of chromium to iron ratio above 2.3 can be smelted to produce a metal containing from 2 to 10 per cent silicon and less than 6 per cent carbon, or a metal containing from 40 to 50 per cent silicon and less than 1 per cent carbon. A metal containing between 10 and 40 per cent silicon and from 4 to 1 per cent carbon can also be made, if desired.

When reducing high chromium, low iron ores, to make an intermediate alloy according to the invention, it has been in many cases found advantageous to mix with the chrome ore a substantial proportion of siliceous iron ore, thus lowering the chromium-iron ratio of the ore charged to the furnace and yielding upon reduction a low chromium ferrochrome metal having a substantial silicon content and a controlled low carbon content. As stated, these relatively high iron ferrochrome silicon alloys have been found useful as intermediate source materials for suppying chromium in the low chromium finished alloys.

Outstanding among the advantages of the process as described are

(1) High yield of chromium metal from ore of any grade without increase of carbon content

(2) Relatively high silicon content in the metal protecting the chromium against oxidation in making chromium alloy steel

(3) Utilization of low chromium high iron ores without disadvantage and with positive advantages

(4) Continuous and regular furnace operation

(5) Economy in materials and labor

(6) Production of siliconized ferrochromium of desired grade.

In making a stainless steel containing less than 20 per cent chromium with iron above 80 per cent, it has been found advantageous to smelt a siliceous iron ore with a chromite ore and coke and lime so as to prepare a silicon alloy containing a low ratio of chromium to iron which is, however, somewhat higher than that required in the finished alloy. Both the silicon and carbon in this intermediate alloy are readily oxidized in a refining step by iron oxide, the reduced iron increasing the iron-chromium ratio in the finished steel. This differs from standard practice in preparation of the intermediate alloy having a ratio of chromium to iron proportioned to that of the finished steel. Any grade of chrome ore is available and the iron ratio of the intermediate alloy is adjusted by addition of siliceous iron ore.

In a typical embodiment of the invention I make an alloy for refining to stainless steel by utilizing a low grade chrome ore and a relatively low grade iron ore, the chrome ore and iron ore used having the following analyses:

	Chrome ore		Iron ore
	Percent		*Percent*
Cr_2O_3	25.7	Fe_2O_3	50
FeO	16.10	SiO_2	43
SiO_2	17.75	Al_2O_3	.97
Al_2O_3	9.00	CaO	.39
MgO	18.35	Mn	.17
CaO	5.67	P	.058
CO_2	6.00	S	.008

Mixing these ores in a proportion of 1435 pounds chrome ore and 1390 pounds iron ore (a ratio of 50.8:49.2) with 420 pounds coke (85 per cent carbon) and 911 pounds lime (CaO), the mixture is fed to a submerged arc furnace having a carbon bed and the charge in the furnace is melted at a temperature approximating 1700° C. At this temperature the melt is freely fluid and reduced metal commences to separate as a bottom layer with an overlying layer of liquid slag. The furnace is fed continuously with a charge mixture of the proportions stated and the slag soon comes to a fairly constant composition as follows:

	Per cent
SiO_2	29.5
Al_2O_3	6.0
CaO	48.6
MgO	14.0
Cr_2O_3	0.5 to 0.75
FeO	Traces

A metal is produced analyzing 24.3 per cent Cr, 4.34 per cent C, and 5.10 per cent Si, with the balance 66.26 per cent principally iron. The yield of metal from the above ore charge is 1145 pounds with slag about 1700 pounds.

This metal containing iron and chromium in a ratio approximating 73 per cent iron to 27 per cent chromium is suitable for refining to stainless steel by known processes in which the carbon and silicon are oxidized by metallic oxides.

In the above example a mixture of chrome ore and iron ore is utilized. It is possible and sometimes advantageous and economical to smelt chromiferous slags containing iron or mixed with iron ores supplying excess silica for reduction. Waste materials containing chromium and iron oxides can thus be utilized in making intermediate ferrochrome alloys.

In another example of the invention a relatively poor chromite ore containing 23 per cent chromium and 31 per cent alumina with a chromium-iron ratio about 2.4 was reduced to a ferrochrome silicon metal with a yield in the metal of about 97 per cent of the chromium of the ore. The ore analysis was:

	Per cent
Cr_2O_3	34
FeO	12
Al_2O_3	31.4
SiO_2	6.5
MgO	14.2
CaO	1.8

The mixture proportions charged to the submerged arc furnace were:

	Pounds
Ore	1000
Coke (85 per cent carbon)	244
Limestone (53 per cent CaO)	128
Quartz (99 per cent SiO_2)	147

From this furnace charge the produced metal,

as tapped, amounted to 357 pounds and averaged 63 per cent chromium, 10 per cent silicon and 3 per cent carbon, with the balance iron; the chromium-iron ratio being 2.2. The accompanying slag weighed approximately 680 pounds and had a lime and magnesia equivalent ratio of about 2.1 parts lime to 1 part silica. The slag contained 1 per cent chromium.

The process, utilizing high grade chromite, produces ferrochromium of standard high Cr/Fe ratio having higher silicon content than the low chromium intermediate alloys; the high silicon being associated with lowered carbon content in high chromium metal.

In the operation of the submerged arc electric furnace in accordance with the invention, the charge, as it is introduced into the furnace, builds up around the electrodes and floats on the surface of a molten bath of metal and slag, the metal settling to the bottom. Smelting of the charge takes place above the slag layer. In being smelted the charge moves progressively downwardly, the slag forming materials and the oxides of chromium and iron melting and passing downwardly toward the molten bath. The excess coke of the charge remains solid and as the charge progresses downwardly the coke is concentrated and forms above the slag layer a porous reducing layer forming an active smelting zone through which the molten charge materials trickle downwardly in passing to the bath. The carbon of the porous coke layer functions to reduce iron and chromium oxides as well as the excess silica associated with the slag forming materials.

When the coke is present in sufficient amount and the temperature of operation is sufficiently high, reduction of silica in excess of the stated slag ratio proceeds with substantial certainty. By maintaining the conditions recited herein with establishment of a fluid slag layer, of the composition noted, on the surface of the molten metal, operation of the furnace is smooth, and uniform conditions are maintained substantially automatically. Slag containing lime and silica in a ratio within the range of from 1.7:1 to 2.2:1 is produced continuously during operations of the furnace and it may be withdrawn either continuously or intermittently.

This application is a continuation-in-part of my application Serial No. 165,954, filed September 27, 1937.

What I claim is:

1. A process of making ferrochrome silicon of controlled silicon and carbon contents by reduction of chrome iron ore with carbon which comprises smelting the ore in a submerged arc electric furnace in the presence of lime and with silica present in excess of the amount required to form with the lime present in the charge a slag having a ratio of lime to silica equivalent to about 1.7 to 2.2 parts by weight of lime to one part of silica, reducing the iron and chromium of the ore and the silicon of the excess silica, and withdrawing from the furnace molten ferrochrome silicon and molten slag containing lime and silica in the stated ratio.

2. In reducing a chromite ore with carbon to obtain ferrochromium metal containing silicon and carbon and a separated slag containing gangue of the ore, a method of increasing the metal yield and controlling the carbon content which comprises smelting the ore in a submerged arc electric furnace with lime, silica and carbon in relative quantities required to form a slag containing lime and magnesia in a ratio to silica equivalent to about 1.7 to 2.2 parts lime by weight to one part silica and to provide an excess of silica over said ratio and carbon in excess of that required to reduce the chromium and iron of the ore and said excess of silica and withdrawing from the furnace said slag in a molten condition and a molten metal alloy of chromium, iron, silicon and carbon.

3. In reducing a chromite ore with carbon to obtain ferrochromium metal containing silicon and carbon and a separated slag containing gangue of the ore, a method of increasing the metal yield and controlling the carbon content which comprises smelting the ore in a submerged arc electric furnace with lime, silica and carbon in relative quantities required to form a slag containing lime and magnesia in a ratio to silica equivalent to about 1.7 to 2.2 parts lime by weight to one part silica and to provide an excess of silica over said ratio and carbon in excess of that required to reduce the chromium and iron of the ore and said excess of silica, the smelting temperature being allowed to rise to a point at which said slag is a free running molten liquid, and withdrawing from the furnace said slag in a molten condition and a molten metal alloy of chromium, iron, silicon and carbon.

4. The process of claim 1 wherein the excess of silica is sufficient in amount to produce a metal containing from 1 to 10 per cent silicon and less than 6 per cent carbon.

5. The process of claim 1 wherein the excess of silica is sufficient in amount to produce a metal containing from 40 to 50 per cent silicon and less than 1 per cent carbon.

6. In making from chromite ores an intermediate ferrochrome alloy as a source of chromium for oxidation-resistant iron-chromium alloys, a process which comprises smelting the ore in a submerged arc electric furnace in admixture with a siliceous iron ore and an excess of carbon over that required to reduce the chromium and the iron of both ores, and withdrawing from the furnace a molten chromium-iron-silicon-carbon metal alloy and a slag having a lime-silica ratio about 1.7 to 2.2 to 1 by weight.

7. A process of utilizing low grade chromium ores of high iron content as a source material for making iron-chromium alloys which comprises smelting such an ore with lime and silica in proportions fluxing the ore gangue to a slag having a base-acid ratio equivalent to 1.7 to 2.2 parts by weight of lime to one part silica and an excess of silica over said ratio together with carbon in excess of that required to reduce the chromium and iron of the ore and the excess of silica over said slag ratio, thereby producing an alloy of chromium, iron, silicon and carbon.

8. In utilizing low grade chromite ores, a method of making such ores available for production of chromium-iron alloys which comprises making an intermediate iron-chromium-silicon-carbon alloy by smelting said ore with a siliceous flux and sufficient carbon as reducing agent to reduce the chromium and iron oxides of the ore and a substantial proportion of silica and to form a normal dibasic silicate slag and separating the slag from said intermediate alloy metal.

MARVIN J. UDY.