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PREPARATION OF FERRO-CHROMIUM IN  
BLAST FURNACES

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6 Claims. (Cl. 75—127)

This invention relates to the pyrometallurgy of ores containing substantial amounts of chromium, and is concerned with the production of alloys containing chromium, e. g., an alloy of chromium, iron and carbon of at least about 35% chromium content, by smelting in the blast furnace an ore containing chromium and another metal, e. g., iron.

This application contains subject matter in common with that of, and is a continuation-in-part of, application Serial No. 252,448 filed January 23, 1939, by Percy H. Royster, entitled "Production of ferro-chromium," now Patent No. 2,238,078.

According to the aforesaid copending application the mechanical difficulty of liquefying refractory chrome ores for smelting the same in the blast furnace can be met by smelting the chrome ore in a blast furnace blown with natural atmospheric air preheated sufficiently high to raise the temperature of the solids in the combustion zone to an extent such that liquefaction of the ore particles is effected and a sufficient superheat above the solidus is attained to cause the fused ore to flow into chemically reactive contact with the solid carbon and thereby to effect reduction of the  $\text{Cr}_2\text{O}_3$  content of the ore at a rate consistent with the rate of descent of the ore particles into the combustion zone of the furnace. For this result blast temperatures of the order of 2000° F., more or less, were recommended.

I have now found that the difficulties resulting from the refractoriness of chrome ores can be avoided also by decreasing the  $\text{Cr}_2\text{O}_3$  content of the burden, e. g., by the addition to the burden of a suitable relatively fusible mineral diluent or carrier, such as a blast furnace slag (preferably a neutral blast furnace slag or one which is only slightly acidic or basic), in a suitable proportion such that the fusibility of the resulting mixture of ore and diluent is within the smelting capacity of the combustion zone of the blast furnace when blown with air preheated to the temperature available. Theoretically, if blast temperatures in excess of 1800° F. are available, the amount of added mineral diluent may be reduced to nil (in which event the process coincides with that of the copending application Serial No. 252,448), although even when hot blast at 1800° F. is available the operating advantages resulting from the incorporation of a substantial amount of the relatively low fusing mineral diluent into the charge strongly recommend the latter procedure. But where the available blast temperature is substantially below the value just mentioned use of the

diluent is (as will be explained more fully hereinafter) a necessity.

In carrying out the improved process of the present invention I prefer to use as the mineral diluent a composition which when combined with the irreducible oxides of the ore produces a final slag that is neither materially basic nor materially acidic. If the available diluent of desired fusing temperature is one which when combined with the irreducible oxides of the ore would produce too basic a final slag, silica or an equivalent "acidic" slag-former (or mixture of two or more such acidic slag-formers) should be added to the burden of ore and diluent whereby substantially to balance the "bases" and "acids" of the final slag: if too acid, the convenient diluent should be balanced by an appropriate addition of lime, magnesia, limestone, dolomite, dolomitic limestone, or equivalent "basic" slag-former.

It is to be understood from the foregoing that the relatively low-fusing mineral diluent need not be a pre-formed slag (e. g., blast furnace slag), but rather that it may, if one so prefers, be a mixture of materials which when fused yields the metallurgical equivalent, or functional equivalent, of a relatively neutral blast furnace slag. Such raw materials of the eventual mineral diluent may include: sandstone, quartzite, argillaceous minerals such as the clays and mica, limestones, and the like, suitably selected and proportioned to yield the desired slag composition. In this connection the following observations are made: Where a high chromium alloy product is desired, the mineral diluent (or, the metallurgical equivalent thereof) must be poor in reducible oxides, particularly in iron oxide and manganese oxide. Many metallurgical slags, produced by other operations than the blast furnace smelting of iron ores to pig iron, exhibit higher iron, or manganese, contents than may be desirable for inclusion in the burden from which the high chromium alloy is to be produced. Accordingly, I may, and preferably do, carefully select the diluent from slags poor in the more readily reducible oxides (e. g., iron oxide, manganese oxide, etc.), balance the "acids" and "bases" by appropriate additions (as described above), and then recycle the resulting final slag as the mineral diluent addition of a subsequent charge, discarding a quantity of the final slag which substantially equals the irreducible oxides content of the ore and coke employed, in order that the volume of diluent may remain substantially constant. Where recycling of the slag is resorted to, care should be taken to avoid reduc-

tion of  $\text{SiO}_2$ , in order to prevent any substantial concentration of  $\text{Al}_2\text{O}_3$  in the recycled diluent.

The practical working of this improved process may be exemplified by the following:

In Example I of application Serial No. 252,448 there was described a blast furnace operation wherein a New Caledonia chromite (chrome) ore, having the analysis:

	Per cent
$\text{Cr}_2\text{O}_3$	54.5
$\text{FeO}$	17.7
$\text{MgO}$	8.0
$\text{Al}_2\text{O}_3$	11.1
$\text{SiO}_2$	3.1
Cr	37.3
Fe	13.8

was smelted in a blast furnace provided with hot blast stoves and equipment capable of blowing the charge with atmospheric air preheated to extraordinarily high temperature (e. g., to as high as 2400-2600° F.). The minimum point of liquefaction of the ore was 3372° F. In that operation, the furnace was charged at 20-minute intervals with rounds comprising 3000 pounds of coke carrying a burden of 4210 pounds of the aforesaid New Caledonia ore, 695 pounds of limestone, 430 pounds of quartzite rock, 214 pounds of slag from a prior operation, and 160 pounds of sintered flue dust (likewise from a prior operation of the furnace). The furnace was blown with 7650 cu. ft./min. of atmospheric air, at 4.5 lbs. pressure (gauge) preheated to 1800° F. The furnace, in that operation, cast 39,600 pounds of metal at 6-hours intervals, and flushed 6950 pounds of slag at hourly intervals. The metal analyzed:

	Per cent
Cr	63.64
Fe	27.35
Si	1.35
C	7.37
S	0.05
P	0.24

and the slag analyzed:

	Per cent
$\text{SiO}_2$	27.94
$\text{Al}_2\text{O}_3$	24.00
$\text{MgO}$	16.28
$\text{CaO}$	20.80
$\text{Cr}_2\text{O}_3$	10.34
$\text{FeO}$	0.27
S	0.78

In applying the concepts of the present invention to the foregoing operation, the furnace was charged at 15 minute intervals with rounds consisting of 2600 pounds of coke; 2000 pounds of the New Caledonia ore, fluxed with 1450 pounds of limestone and 500 pounds of quartzite rock; and 4000 pounds of blast furnace slag (making a ratio of two of slag to one of ore). This slag had approximately the following analysis:

	Per cent
$\text{SiO}_2$	34.5
$\text{Al}_2\text{O}_3$	15.0
$\text{CaO}$	36.7
$\text{MgO}$	11.6
S	1.5

The furnace was this time blown with 9750 cubic feet per minute of atmospheric air, containing 3.54 grains of moisture per cubic foot, and preheated to 1200° F. The furnace cast 25,250 pounds of metal at 6-hour intervals, and flushed

24,000 pounds of slag at hourly intervals. The metal analyzed:

	Per cent
Cr	62.93
Fe	27.39
Si	1.15
C	7.65
S	0.10
P	0.08
Mn	0.70

and the slag analyzed:

	Per cent
$\text{SiO}_2$	33.67
$\text{Al}_2\text{O}_3$	14.83
15 CaO	36.28
MgO	11.47
$\text{Cr}_2\text{O}_3$	2.04
FeO	.52
MnO	.53
S	1.32
Cr	1.40

The temperature of the metal and slag remained substantially the same as in the prior operation. This time, however, the top gas analyzed (percent by volume):

	Per cent
$\text{CO}_2$	2.8
CO	36.6
30 $\text{H}_2$	1.7
$\text{N}_2$	58.9

Since the slag made has substantially the same composition as the diluent blast furnace slag charged, it was crushed and recharged in a later operation. By recycling the slag and making use of its chromium content the resulting metal then became a higher grade alloy and analyzed:

	Per cent
Cr	64.73
Fe	25.95
Si	1.15
C	7.70
S	0.10
P	0.07
Mn	0.30

It will be seen, from the above specific application of the concept of this invention, that by the expedient of using a material amount of relatively readily fusible mineral diluent with the chromite ore of the burden the ore was liquefied at a materially lower temperature than that found necessary in the carrying out of the parent process and a desirably complete reduction of chromium oxide was had. While it is true that somewhat more coke (per unit weight of metal produced) was required, this expense is more than offset by the fact that the process was operable using conventional hot blast stoves and blowing equipment which later would have been incapable of providing the superheated blast required for the carrying out of the parent process.

My researches have demonstrated that there is a relationship between the amount of dilution (with the aforesaid mineral diluent) required and the blast temperature available. Thus, with reference to the foregoing example, where a blast temperature of 900° F. is all that is available, I find that the process is operable using such hot blast provided three to seven parts (by weight) of the relatively readily fusible mineral diluent are employed per one part of the chrome ore. Although the economic results are not attractive, because of excessive coke consumption and by reason of decrease in chromium recovery due to

excessive slag volume,—the process may be worked with essentially cold blast where sufficient coke is employed and a sufficiently great addition of the readily fusible diluent is made: in such extreme case it is unsafe to employ less than 10, and preferably between 10 and 20, parts of diluent per one part of ore. Thus, the concept of bringing the chrome ore into chemically reactive contact with solid carbon, for effecting the smelting of the same in the blast furnace, with the aid of a substantial addition of readily fusible mineral diluent is operable throughout the full range between essentially cold blast,—as one extreme,— and a highly superheated blast as the other extreme: the higher the blast is preheated the smaller the amount of mineral diluent addition necessary for complete liquefaction of the ore, and vice versa.

I claim:

1. In the process of producing ferro-chromium involving the operations of charging into a blast furnace solid carbonaceous fuel and a burden consisting essentially of a chrome ore having a substantially high chromium content and blowing the charge with atmospheric air, the improvement which consists in diluting the concentration of the chrome ore in the charge by the addition to the latter of a slag-forming mineral diluent having a fusing point materially lower than that of said chrome ore and consisting predominantly of oxides of silicon, aluminum, calcium and magnesium and low in reducible oxides such as the oxides of iron and manganese, the composition of the mineral diluent being so chosen, with respect to the composition of the gangue of the chrome ore, that when said mineral diluent is combined with the gangue the two produce a substantially neutral final slag, the amount of mineral diluent so added being at least as great as that of the chrome ore.

2. In the blast furnace smelting of chrome ore to ferro-chromium, the step which consists in di-

luting the concentration of chrome ore in the charge by the addition to the latter of blast furnace slag in an amount at least as great as that of said ore.

- 5 3. In the blast furnace smelting of chrome ore to ferro-chromium, the step which consists in diluting the concentration of chrome ore in the charge by the addition to the latter of substantially neutral blast furnace slag, the amount of such addition being inversely proportional to the extent of preheat of the blast.
- 10 4. In the improved process defined in claim 2, the step which consists in balancing acids and bases in the resulting final slag whereby the latter is maintained substantially neutral by the addition to the burden consisting essentially of ore and diluent of an appropriate slag-former capable of influencing in the desired direction the bases-to-acids ratio of said final slag.
- 15 5. In the improved process defined in claim 1, the step which consists in recycling a substantial proportion of the resulting final slag as the relatively readily fusible mineral diluent addition of the charge.
- 20 6. Cyclical blast furnace process of producing ferro-chromium from chrome ore which comprises charging the furnace with coke and a burden consisting essentially of a mixture of the ore and at least as much readily fusible substantially neutral blast furnace slag as ore, blowing the charge with atmospheric air, adjusting the proportion of coke to mixed burden and the temperature of the blast with relation to the liquefaction temperature of the mixed burden to insure substantially complete liquefaction of the latter, withdrawing from the furnace at a point beneath the combustion zone the resulting slag and the resulting metal, and returning the resulting slag to the furnace charge as the mineral
- 25 30 35 40 diluent component of the burden thereof.

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