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METHOD OF PRODUCING LOW CARBON
CHROMIUM-CONTAINING IRON ALLOYS

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This invention relates to metallurgy and more particularly to chromium-containing iron alloys. In the manufacture of such alloys it is customary to first form a molten bath of iron and to add the chromium thereto in the form of ferro-chromium, an alloy of iron and chromium in which the chromium content preferably approximates 70% but may vary within the range 60 to 80%. For many reasons, well known in the art, it is highly desirable to employ a ferro-chromium alloy that is relatively low in carbon.

One of the objects of this invention is to provide an improved method of producing a low carbon ferro-chromium alloy. Another object is to provide an improved method of producing chromium-containing iron alloys. Still another object is to provide an economically practical method for the production of high grade low carbon ferro-chromium from low grade chromium-containing ores. Other objects and advantages will be apparent as the invention is more fully hereinafter disclosed.

In accordance with these objects, I have discovered that ferro-chromium alloys high in carbon may be effectively decarburized and rendered low in carbon by fusing the same with chromium oxide in a substantially non-oxidizing atmosphere, and preferably in the presence of a flux having at least a low solubility towards the chromium oxide.

I have also discovered that the rate of decarburization of said ferro-chromium may be increased markedly by reducing the pressures of the non-oxidizing atmosphere to below normal pressures, or by vigorously agitating the molten bath or by employing both expediences simultaneously.

I have found that in a substantially non-oxidizing atmosphere the carbon content of molten ferro-chromium will react slowly with chromium oxide initially at a temperature as low as about 1600° C. but that at temperatures within the range 1800-1900° C. the reaction is more rapid and will proceed at an economically practical rate with an evolution of carbon monoxide until the major portion of the carbon has been removed from the molten metal.

I have further found that by inhibiting the formation of excessive amounts of carbon dioxide, by enclosing the surface of the bath from the atmosphere or by maintaining a strongly hydrogenous atmosphere over the surface of the bath, or both, the rate of carbon removal by the reduction reaction of the carbon in the molten metal with the chromium oxide becomes suf-

ficiently rapid to be economically practical. However, by vigorously stirring the bath or by operating under reduced pressures or both the rate of carbon removal may be greatly accelerated.

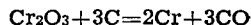
I have further found that by the use of a surface covering flux comprised of relatively non-volatile compounds which will dissolve or form carbon-reducible compounds with the chromium oxide, the rate of carbon removal may be still further increased.

In the practice of the present invention, I have found that by first finely pulverizing the high carbon ferro-chromium alloy and mixing therewith the chromium oxide and the flux, forming the mixture into briquets and then fusing the same, the removal of the carbon in a non-oxidizing atmosphere is effected at such a rate that neither vigorous agitation nor reduced pressures is necessarily required to render the process economically practical although either or both means may be employed, particularly in the later stages of decarburization to effect the more economical elimination of the final fractional percentages of the carbon.

The discoveries hereinabove set forth may be widely adapted without essential departure from the present invention, as one skilled in the art will perceive.

As one specific embodiment of the present invention, I will disclose the same as it is applied to the decarburizing of high carbon ferro-chromium.

The ferro-chromium alloy is first ground to pass about 100 mesh and chromium oxide (Cr_2O_3) of approximately the same degree of fineness is mixed therewith in an amount in slight excess of the theoretical amount required to combine with all of the carbon content of the alloy in accordance with the equation given below:



A flux, such as calcium fluoride, in an amount approximating one-third ($\frac{1}{3}$) that of the chromium oxide added also is added, and the three materials after thorough mixing together are briquetted into briquets of any convenient or desired size using glucose or similar thermally decomposable organic binder and dried.

The dried briquets are then charged into an electric arc furnace of the indirect arc type and provided with a cover enclosing the hearth from the atmosphere, except for gas inlet and outlet openings, and are slowly heated therein to fusion and to temperatures at least approximating 1600°

C. and preferably within the range 1800-1900° C. This temperature is maintained for a time interval necessary to eliminate the major portion of the carbon (80% thereof) and where a lower carbon content is desired the molten bath is heated to higher temperatures within the range 1900-2200° C.

At temperatures within the range 1800-1900° C., I have found that it is not usually necessary to introduce any other atmosphere in the furnace particularly during the early stages of decarburization and also when relatively high carbon ferro-chromium (4 to 6% carbon) is being treated. As the carbon content of the bath decreases to below about 2%, I have found it advisable to introduce hydrogen in the furnace to maintain a strongly reducing atmosphere over the surface of the bath.

I have also found it advisable to maintain a temperature above about 1900° C. as the carbon content of the bath is lowered to below about 1% in addition to the maintaining of a non-oxidizing atmosphere over the surface of the bath.

As the carbon content of the bath falls to below about .50%, the rate of carbon removal even at 1900-2200° C. becomes quite low and a strongly hydrogenous atmosphere substantially free of carbon dioxide, nitrogen, water vapor and oxygen should be maintained over the surface of the bath to insure the removal of the carbon to .10% and below within an economically practical time interval, and to inhibit reoxidation of the chromium.

As an example of the practice of this mode of procedure, ferro-chromium analyzing 68.97% chromium, 5.84% carbon, balance iron, when ground to about 100 mesh and mixed with chromium oxide (Cr_2O_3) and fluorspar (CaF_2) in the ratio of 26 pounds of oxide and 8 pounds of fluorspar to each 100 pounds of ferro-chromium, and then briquetted using a 25% glucose aqueous solution as a binder and dried, was converted into a ferro-chromium alloy analyzing 80% chromium and only .18% carbon when fused and treated as hereinabove described.

The low carbon ferro-chromium alloy thus produced is admirably suited for use in the forming of low carbon iron and steel alloys, as one skilled in the art will perceive.

As a modification of the present invention, I may first produce a high carbon ferro-chromium by reducing a mixture of iron and chromium oxides with carbon as heretofore practiced in the art, employing as a source of the iron and chromium oxides, ores which ordinarily are considered of too low a chromium content for economical reduction and using a sufficient excess of carbon so that on subsequent treatment of the high carbon ferro-chromium alloy produced in accordance with the present invention, the chromium additions made thereto as a result of decarburization by chromium oxide reduction will be sufficient to raise the chromium content of the ferro-chromium to within the range 60-80% usually desired for such alloys.

As another modification of the present invention, the production of a high carbon ferro-chromium, as hereinabove disclosed using relatively low grade chromium ores, the decarburization of the same, and the manufacture of chromium-containing iron and steel alloys incorporating the decarburized ferro-chromium may be combined in one manufacturing process, which

would evidence great economies over the processes now in use.

For example, in the manufacture of stainless chromium-iron and chromium-nickel-iron alloys, it is customary practice to first form a low carbon substantially pure molten iron bath and to add thereto the ferro-chromium and other alloying constituents desired. In such a process the carbon content of the ferro-alloys added materially increases the carbon content of the final alloy. Where a final carbon content of below .10% is desired in such alloys, it is obvious that the carbon content of the molten iron bath must be brought to a percentage below .10% that when added to the total carbon of the ferro-alloys added does not exceed .10%. This normally produces an iron bath having an oxygen content that is sufficient to cause excessive losses in alloyed constituents added requiring deoxidation prior to such alloy additions. Moreover, such low carbon ferro-alloys are expensive additions and the obtaining of a molten bath of iron of the requisite low carbon content is expensive and time consuming and the use of deoxidizing agents materially raises the cost of such alloys.

By the practice of the present invention, however, much of the cost can be eliminated, first by the use of the less expensive chromium-containing ores in the manufacture of a high-carbon ferro-chromium and secondly by the use of low carbon ferro-chromium prepared in accordance with the present invention and thirdly by the production and use of moderately low carbon iron in the forming of the chromium-containing iron alloy desired.

For example, the low carbon ferro-chromium produced in accordance with the present invention either by decarburizing high grade ferro-chromium (60-80% Cr) or by first producing a low grade high carbon ferro-chromium alloy (below 60% Cr) and then decarburizing and converting the same simultaneously into a high grade ferro-chromium alloy, as hereinabove described, may be added while still molten to a molten bath of low carbon substantially pure iron prepared, for example, by the standard open hearth practice and having a carbon content of about .10% (or less) in an amount sufficient to obtain a total Cr content of 12-18% to impart the stainless characteristics desired without material increase in the carbon content of the iron. In the presence of sufficient ferro-silicon or ferro-manganese or both the chromium losses by oxidation would be reduced to a minimum. Additions of other desired alloying elements, such as Ti, Mo, W, Ta and Nb in the form of ferro-alloys, also can be made thereto in the small percentages normally utilized without material increase in the carbon content of the alloy.

Stainless chromium-nickel-iron alloys may be similarly prepared in an economically practical manner, as one skilled in the art may perceive, as well as any of the chromium-containing iron alloys known in the art.

Having hereinabove described the present invention generically and specifically and given several specific embodiments of the same, it is believed apparent that the same may be widely varied without essential departure therefrom and all such modifications and departures are contemplated as may fall within the scope of the following claims.

What I claim is:

1. The method of decarburizing a carbon-con-

taining iron-chromium alloy which comprises subdividing the alloy to pass about 100 mesh, mixing therewith chromium oxide of about the same particle size in an amount in slight excess of the theoretical amount to combine with all 5 of the carbon content of the said alloy, adding a flux comprised at least in part of an alkaline earth metal fluoride therewith in an amount approximating one-third of the amount of chromium oxide added, compacting the mixture into 10 briquets and then heating the briquets on a hearth enclosed from the atmosphere to fusion and to temperatures within the range 1600-2200° C. for a time interval at least sufficient to complete the reaction of the carbon content of the 15

alloy with the chromium oxide maintaining during said reaction time interval a non-oxidizing and reducing atmosphere over the said fused bath at atmospheric pressures.

2. The method of claim 1, wherein as the carbon content of the molten metal decreases below about 1% a hydrogenous atmosphere is maintained over the surface of the bath.

3. The method of claim 1, wherein as the carbon content of the molten metal decreases below .50% a hydrogenous atmosphere substantially free of carbon dioxide, nitrogen, water vapor and oxygen is maintained over the surface of the bath.

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