United States Patent Office
3,595,709
Patented July 27, 1971

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3,595,709

PROCESS FOR PRODUCING FERROCHROME ALLOYS WITH HIGH NITROGEN CONTENT AND LOW CARBON CONTENT

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No Drawing. Filed Mar. 4, 1968, Ser. No. 709,892
Claims priority, application Italy, Mar. 7, 1967, 13,446/67
Int. Cl. C21d *5/10*; C22c *39/14*
U.S. Cl. 148—16 7 Claims

ABSTRACT OF THE DISCLOSURE

Ferrochrome alloys high in nitrogen (which may be as high as about 15%) and low in carbon (which may be as low as about 0.3%) are made by treating pulverized ferrochrome up to 8% in carbon with a stream of gas comprising ammonia at temperatures of the order of about 500° to 800° C. The gas treatment may be carried out by the fixed bed method or the fluidized bed method.

This invention relates to a process for the production of ferrochrome alloys having a high nitrogen content and a low carbon content.

It is well known that ferrochrome alloys are used on a vast scale in the metallurgic field. The numerous uses of ferrochrome alloys in this field include also the use of said alloys as a means for bringing the nitrogen content up to a 0.3% in certain kinds of chrome steels, with the aim of improving some of their properties (tensile strength, machinability, weldability, intercrystalline corrosion resistance, etc.). In order for the ferrochrome alloy to bring about this result it is necessary that it have certain compositional characteristics, as for example a low carbon content, since the final content of carbon in and above-mentioned chrome steels does not commonly exceed 0.3%.

According to previously known techniques nitrided ferrochrome can be presently obtained:

(a) By nitriding ferrochrome in molten state, such as is obtained by alumino-thermal or silicothermal processes and consequently having a very low carbon content. The nitriding is carried out by adding solid nitrates or by blowing in nitrogen. A nitrogen content not higher than 2% is reached by means of this process.

(b) By nitriding solid ferrochrome—finely ground and having a low carbon content (maximum, 0.1%)—with ammonia or nitrogen. A nitrogen content up to a maximum value of 10% can be reached by means of this process.

One object of the present invention is to provide ferrochrome alloys with a very high nitrogen content which can reach a value as high as 15%. Such a nitrogen content is from two to seven times higher than the content of other ferrochrome alloy products presently available on the market.

Another object of this invention is the employment, as the starting material for obtaining the desired nitrided ferrochrome alloys, ferrochrome alloys having a high carbon content—which indeed can be as high as 8%—without the necessity for any preliminary decarburization.

The high nitrogen content of the ferrochrome alloys obtainable by the process of the present invention offers the remarkable advantage of making the use of a ferrochrome alloy, as steel nitriding agent, substantially independent—at least within certain limits—of considerations of its carbon content. If in fact one compares the attainment of equal final nitrogen content in a certain steel by starting from the ferrochrome alloys commonly on the

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market (which therefore have a low nitrogen content) or by starting from the ferrochrome alloys produced according to the process of the present invention, the significantly smaller quantitative requirement of the latter alloys becomes quite clear.

It follows that the carbon content need not necessarily be maintained at a very low value. The carbon increase in the steel will be maintained within acceptable limits even if use is made of a starting ferrochrome alloy with 1% carbon content.

Starting for example from a ferrochrome alloy produced according to the present invention and having a 15% nitrogen content as well as 0.9% carbon, for reaching a final nitrogen value in the steel of 0.3% it is sufficient to add (without considering the possible losses of nitrogen) 2 gr. ferrochrome alloy per 98 gr. steel. The carbon increase given by the alloy is in this case equal to 0.018%.

These and other objects of the present invention can be attained by a process which consists in treating carburized ferrochrome, having a medium or high carbon content, with a gaseous ammonia stream without the necessity of a preliminary decarburization. The value of 8% can be taken as the top value for the carbon content, since increasing the percentage of carbon beyond that value favors the presence of carbon in a diffcultly eliminable form. It is therefore generally preferable to treat carburized ferrochrome alloys having a carbon content lower than 5%.

The reaction is carried out in thermoregulated tube furnaces, made of or lined with refractory material, at times varying in dependence on both the carbon content of the starting material as well as the carbon content desired in the final product and also on the operational conditions of the nitriding stage.

The ferrochrome alloy starting material, pulverized to less than 10 mesh (and preferably 70 mesh or less), is subjected to the action of ammonia either by simply heating the alloy within the gaseous stream using the fixed bed method, or by heating the alloy using the fluidized bed method. (The mesh sizes referred to herein are on the A.S.T.M. scale.)

By the first method, the alloy starting material reposing on the bottom of the tube furnace, placed horizontally, is steadily kept stirred by means of suitable agitators in order to expose the maximum surface of contact to the action of the ammonia gas reactant. In this instance, the duration of treatment of a common carburized ferrochrome, containing from 4 to 6% carbon, ranges from a minimum of 6 hours—for producing a final product containing about 2% carbon and 12% nitrogen—to the maximum of 40 hours—for producing a final product with carbon below 1% and 15% nitrogen.

By the second method, the carburized ferrochrome alloy starting material is suspended in a fluidized bed, the gaseous stream used for maintaining said bed being the reacting gas itself or nitrogen. By employing the fluidized bed technique the duration of the treatment is remarkably reduced.

Throughout the nitriding stage the reaction temperature is kept at a substantially constant value included between 500° C. and 800° C., and preferably between 600° C. and 700° C.

If desired, it is entirely feasible—starting from carburized ferrochrome—to obtain a ferrochrome having a relatively low nitrogen content as well as a relatively low carbon content. Thus, by subjecting the carburized ferrochrome (after having undergone nitriding via treatment with ammonia in accordance with the main process described in detail herein) to a subsequent heat treatment at a temperature above 1300° C. in an inert gas atmosphere such as argon or hydrogen or under vacuum, it loses substantially all the nitrogen that has become fixed during the earlier treatment and in that way is converted into a ferrochrome alloy low in both carbon and nitrogen.

The following detailed working examples are given in order still better to illustrate this invention:

EXAMPLE 1

5 kg. ferrochrome alloy with content C=4.56%, Cr=68.2%, Si=0.63%, and size smaller than 70 mesh, were arranged in the form of a thin layer on the bottom of a tube type furnace of a refractory (silico-aluminous) material, installed horizontally. The pulverized alloy was heated at 650° C. for 36 hours in a stream of dry ammonia at a flow rate of 12 m.^{3}/hr. 258 g. HCN and 66 g. hydrocarbons, expressed as CH_4, were formed; outlet gases still contained about 15% by volume of NH_3 and the remainder consisted of nitrogen and hydrogen.

The slightly agglomerated ferrochrome which was obtained contained N=15%, C=0.9% and Cr=60.1%.

EXAMPLE 2

5 kg. ferrochrome, also sized less than 70 mesh but with C=2.80%, were treated under the same conditions specified above in Example 1.

After a treatment time of 6 hours the total carbon percentage was lowered to 0.7%, and after 10 hours the residual carbon amounted to 0.35% while the nitrogen content reached a value of 15%.

EXAMPLE 3

2 kg. ferrochrome sized between 325 and 200 mesh, with content C=4.8%, were treated at 650° C. in fluidized bed, with a gas mixture consisting of N_2 and NH_3 in a volumetric ratio of 20:1, streaming with a flow rate of 20 m.^{3}/hr.

The fluidized bed was realized by causing the gaseous mixture to stream upwardly through a 5 cm. long porous diaphragm cemented at the center of a tube of refractory material having a diameter of 10 cm. and made of sintered quartz granules. The gas passed through this porous diaphragm and then through the layer of pulverized ferrochrome alloy while thus maintaining a rather stable fluidized bed. After a treatment time of 3 hours the nitrogenous ferrochrome product contained C=1.4% and N=15%.

EXAMPLE 4

(This example describes the production of a ferrochrome alloy having a low carbon content and a low nitrogen content as mentioned above.)

5 kg. ferrochrome (C=4.8%), treated as described above in Example 3 but for a duration of 8 hours and finally containing C=0.4% and N=15%, were then treated for 3 hours at 1350° C. in an argon atmosphere within a furnace made of a silico-aluminous material.

A metal bar containing C=0.5% and N=0.05% was obtained in this way.

What is claimed is:

1. A process for the production of ferrochrome alloys having a high nitrogen content and a low carbon content, comprising treating a pulverized ferrochrome having a carbon content up to about 8% by weight in a stream of gaseous ammonia at a temperature between about 500° C. and 800° C. with consequent elimination of a large part of the carbon from the starting material substantially in the form of gaseous hydrocyanic acid and simultaneous nitrogen fixation.

2. A process according to claim 1, wherein the ferrochrome alloy starting material is in finely divided form of not more than 10 mesh (A.S.T.M.).

3. A process according to claim 1, wherein the reaction between the ferrochrome starting material and the ammonia is carried out by heating the alloy in an ammonia atmosphere with use of the fixed bed or the fluidized bed method, in this latter case the bed consisting of ferrochrome alloy particles kept in suspension by the reaction gas or nitrogen.

4. A process according to claim 1, wherein the reaction temperature ranges between about 600° C. and 700° C.

5. A process according to claim 1, wherein the nitrogen content of the finished ferrochrome alloy is up to about 15%.

6. A process for the production of ferrochrome alloys having a relatively high nitrogen content and a relatively low carbon content, comprising treating a pulverized ferrochrome having an initial carbon content of from 1% to about 8% by weight in a stream of gaseous ammonia at a temperature between about 500° C. and 800° C. with consequent elimination of a large part of the carbon from the starting material and simultaneous nitrogen fixation to a final nitrogen content of up to about 15%.

7. A process according to claim 1 for the production of ferrochrome alloys having a high nitrogen content of from about 12% to 15% and a low carbon content, comprising treating a pulverized ferrochrome having a carbon content up to about 8% by weight in a stream of gaseous ammonia at a temperature above about 600° C. with consequent elimination of a large part of the carbon from the starting material and simultaneous nitrogen fixation.

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U.S. Cl. X.R.

75—130.5