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FERROCHROME PROCESS AND PRODUCT

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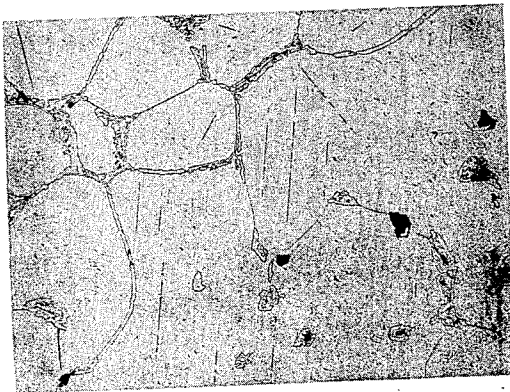


FIG. 1

M.L. 34233 Mag. 100X
Structure at Center of Lump of Nitrided Low Carbon Ferrochromium; Nitrogen Penetration to Center is Indicated by the Presence of the Large and Small Needles

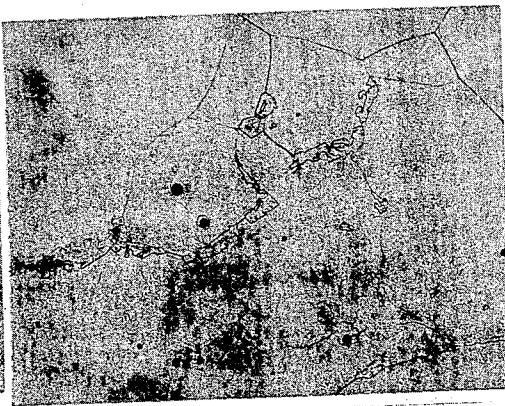


FIG. 2

M.L. 34234 Mag. 100X
Structure of Untreated Low Carbon Ferrochromium
Note absence of large nitride needles.



FIG. 3

M.L. 34233 Mag. 100X
Structure of Surface of Treated Ferrochromium Showing Extent of Nitrided Case

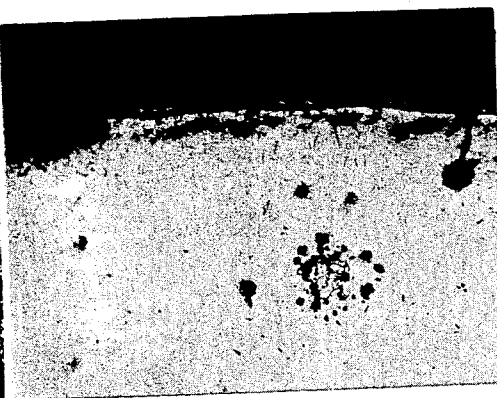


FIG. 4

M.L. 34508 160 X
Photomicrograph of Nitrided Lump 99% Chromium Metal Showing the Presence of a Nitrided Case

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UNITED STATES PATENT OFFICE

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FERROCHROME PROCESS AND PRODUCT

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Continuation of application Serial No. 511,864, November 26, 1943. This application September 16, 1946, Serial No. 697,232

4 Claims. (Cl. 75-176)

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This application is a continuation of our co-pending application, Serial No. 511,864 of November 26, 1943 entitled Ferrochrome process and product, (now abandoned) which application is a continuation in part of our application, Serial No. 404,918 of July 31, 1941 entitled Ferrochrome process (now abandoned) and the invention relates to iron-chromium alloys, more particularly to iron-chromium pre-alloys and to an art of producing the same.

One of the objects of our invention is the production of an iron-chromium pre-alloy of high chromium and nitrogen contents which readily lends itself to an ease of handling and which has a wide range of application in the production of stainless steels of high nitrogen content.

Another object is the production of a high-grade ferrochromium pre-alloy of the type indicated in a simple reliable and thoroughly practical manner at maximum efficiency and minimum expense.

Another object is the direct and economical production of a nitrogen-containing iron-chromium pre-alloy of high nitrogen and chromium contents employing conventional furnacing equipment and handling apparatus.

Other objects will be obvious, in part, and in part pointed out hereinafter.

The invention accordingly consists in the several steps and in the relation of each of the same to one or more of the others as described herein, the scope of the application of which is indicated in the following claims.

In the accompanying drawing, illustrating certain features of our invention,

Figs. 1 and 3 are micrographs of nitrogen-containing ferrochromium produced in accordance with the invention,

Fig. 2 is a similar micrograph of untreated ferrochromium, and

Fig. 4 is a micrograph at further enlargement of chromium metal.

As conducive to a clearer understanding of our invention, it should be noted at this point that ferrochromium pre-alloys serve conventionally as the principal source of chromium in the production of various grades of alloy steel, including stainless steel. This ferrochrome, in the so-called standard grades, contains approximately 70% chromium, but may contain from 40% to 90% chromium.

By the use of nitrogen-bearing ferrochromium, a small percentage of nitrogen is introduced into alloys comprising iron and chromium, to improve certain working properties of the metal and to

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lend refinement to the metal grain structure. In many instances of use, ferrochromium must be very pure to avoid contaminating the metal to which it is added. Where high nitrogen ferrochromium is employed as an addition in stainless steel finishing operations, for example, carbon content of the pre-alloy must be low so as not affect the carbon analysis of the steel to any material degree.

At present, numerous processes are employed in the nitrogenation of molten ferrochromium. For example, high-nitrogen ferrochromium is produced by blowing nitrogen or ammonia through a bath of low-carbon ferrochromium.

In all of these processes, the chromium in the molten ferrochromium takes up nitrogen from a nitrogen-containing material.

Difficult furnacing and pouring operations are encountered in producing nitrogen-bearing ferrochromium by heretofore known processes. The processes, in execution, require considerable equipment, skill and supervision. Processes for the nitrogenation of a molten ferrochromium apply essentially to large scale pre-alloy production, and, therefore, are not suitable for use in the production of small quantities of nitrogen-bearing ferrochromium.

A small percentage of nitrogen also may be introduced into stainless steel by way of chromium nitride. This chromium nitride is prepared by heating finely-divided chromium metal in nitrogen or ammonia at a temperature approximately 850° C. (1560° F.). This finely-divided material is expensive, is difficult to produce, and is difficult to handle in use.

An object of our invention is the provision of a process for the nitrogenation of solid ferrochromium; which enables the production of high-nitrogen ferrochromium without melting available solid ferrochromium; which has little effect upon the carbon content of the pre-alloy, yet permits the introduction of substantial amounts of nitrogen; which allows close control over the amount of nitrogen going into the pre-alloy; which is practiced readily without great cost, requiring a minimum of equipment and supervision; and which gives a clean finished product ready for immediate use.

Referring now more particularly to the practice of our invention, we produce ferrochromium of a high nitrogen content by the nitrogenation of lump ferrochromium. We find that solid ferrochromium, held at a particular high temperature in the immediate presence of nitrogen-containing material, absorbs a considerable amount of nitro-

gen. Nitrogen from the nitrogen-containing material penetrates the surface of solid ferrochromium reacting with chromium in the pre-alloy to form stable chromium nitrides, or perhaps solid solutions.

The avidity of ferrochromium for nitrogen we find increases in direct proportion with the amount of chromium present in the pre-alloy. Further, we find that the amount of nitrogen absorbed by ferro-chromium increases as the time of pre-alloy heating increases. Nitrogen penetrates to greater depths below the metal surface as the period of heating is extended and a ferrochromium product of higher nitrogen content results. For all practical purposes, a period of time ranging from 1 to 6 hours, usually is sufficient to ensure proper reaction of nitrogen with chromium in the pre-alloy.

The amount of nitrogen absorbed per unit of heating time increases when smaller lumps of ferrochromium are employed; the metal surface being greater and, consequently, more chromium in the metal is exposed promptly to the nitrogen-containing materials. On the other hand, extremely small lumps of ferrochromium usually have no practical use in metallurgical operations and accordingly are not commercially available. Ferrochromium is added through a finishing slag to molten metal and when the ferrochromium lumps are extremely small, waste is incurred by the pre-alloy particles being suspended in the finishing slag.

It is interesting to note that the temperature to which solid ferrochromium is heated has an important and material effect upon the total amount of nitrogen the chromium is capable of absorbing. Best results are obtained in the practice of our invention by using heating temperatures falling within the critical temperature range of 1700° F. to 2400° F. A possible explanation for this lies in the fact that chromium reacts differently under different temperature conditions. Different solid solutions of chromium and nitrogen, or perhaps different chromium-nitrogen compounds, form within the range of temperatures below the melting point of chromium or ferrochromium. We do not wish, however, to be bound by this explanation.

As illustrative of the practice of our invention, we procure a suitable quantity of low-carbon ferrochromium comprising about 70% chromium and the remainder iron. This is in lump form, the lumps being approximately the size of a small walnut, that is about one-inch size, thus ensuring a large surface area per volume unit of the pre-alloy. The lump crushed ferrochromium then is put in a nitriding box and placed within a furnace. It is heated at 2000° F. for a period of about four hours in the immediate presence of nitrogen gas. Conveniently the nitrogen is passed into one end of the box by a suitable conduit and out the other end by another conduit. A flow of nitrogen gas over and through the crushed ferrochromium is assured. It is to be understood that ammonia gas, or certain other nitrogen-containing gases may be employed in lieu of nitrogen gas. Good results are achieved where the nitrogen gas used is commercial bottled nitrogen.

A heating period of four hours allows sufficient time for the hot ferrochromium to react with the nitrogen present. Nitrogen gas reacts with the low-carbon ferrochromium, particularly with the chromium and iron of the pre-alloy, forming stable nitrides and perhaps solid solutions. This reaction progresses from the surface of the metal

to within the pre-alloy giving a high-nitrogen ferrochromium product.

It will be seen by referring to the accompanying drawing, Figs. 1 and 3, as compared with untreated ferrochromium, illustrated in Fig. 2, that nitrogen penetrates well into the interior of the lump ferrochromium, this penetration being in the form of large and small needles. This effect is in direct contrast with that of nitriding chromium metal where but a thin case is formed (see Fig. 4).

Upon the expiration of the heating period, we remove the nitrided ferrochromium from the furnace and permit it to cool. After cooling, the high-nitrogen ferrochrome is stored for future use. The pre-alloy is found to contain approximately 1.3% nitrogen.

The nitrogen content for other samples treated at different temperature values are given in the table below:

Sample	Temperature	Time	%N
A	1500° F.	2 hours	.13
1	1800° F.	2 hours	.55
2	2000° F.	2 hours	1.25
3	2200° F.	2 hours	1.09

In accordance with another embodiment of our invention, a suitable quantity of lump crushed low-carbon ferrochromium is placed in a nitriding box and an amount of nitrogen-containing material, such as calcium cyanimide or other nitride which decomposes at relatively low temperatures, is added to the contents of the box. Then the box is closed and put in a furnace where it and its contents are heated at the critical temperature of 1700° F. to 2400° F. for a period of one to six hours. Presumably the iron and chromium of the hot-low-carbon ferrochromium picks up nitrogen from the nitrogen-containing material to form various nitrides or solid solutions as noted above. The box is removed from the furnace upon expiration of the heating period and the nitrided low-carbon ferrochromium, upon being removed from the box, is stored for future use.

An iron-chromium alloy of desired nitrogen content is achieved, as indicated above, by introducing nitrogen into lump ferrochromium. The nitrogen of the nitrogen-containing material goes either into solid solution, or forms stable compounds, with iron and chromium in the ferrochromium to form high-nitrogen ferrochromium. The finished product is in lumps and, therefore, is ready for immediate use, as for example, in the production of nitrogen-bearing stainless steel.

In accordance with our invention, small or large quantities of ferrochromium may be nitrided conveniently. Our finished product is of such lump size that no difficulty or waste is encountered while introducing the material into a steel bath. The pre-alloy sinks into molten metal quite readily even where the introduction is made through a finishing slag. On the other hand, the lumps of ferrochromium used in making our product are sufficiently small to ensure that a very large surface is exposed to the nitrogen-containing material. In fact, under certain circumstances, it may be desirable to crush the ferrochromium to a powder and then heat the powder in the presence of nitrogen at the temperature and for the period of time prescribed hereinbefore. Where this alternative is employed, we find it advisable to mix a suitable binder ingredient with the nitrided ferrochromium powder and then press the material into briquettes. Thus, by briquetting the material, the finished product is handled

easily without waste and, moreover, has greater utility in metallurgical operations because of its increased density.

The carbon content of ferrochromium is not affected substantially by our nitrogenation process. High-nitrogen ferrochromium of both the high-carbon and low-carbon grades may be produced as desired. A high-nitrogen ferrochromium product made by the nitrogenation of solid low-carbon ferrochromium, therefore, has a low-carbon content. The pre-alloy serves very effectively as a steel bath addition metal, where chromium and nitrogen contents of the bath are to be increased without material increase in carbon content. It will be understood, however, that there are certain uses for a high-carbon ferrochromium nitrided according to our invention, especially in making nitrogen additions to the high-chromium steels whose carbon is not such a factor.

While for purposes of illustration, the production of a nitrided ferrochromium of 1.3% nitrogen content is described above, it will be understood that by controlling the amount of nitrogen-containing material used in our process, the nitrogen content of the finished product is altered. The nitrogen content is found to range from 0.7% to 2.0%, the higher nitrogen contents in general being found in the higher chromium ferrochrome.

Thus it will be seen that there has been provided in this invention a ferro-alloy of high nitrogen content and an art of producing the same in which the various objects hereinbefore noted, together with many thoroughly practical advantages, are successfully achieved. It will be seen that our process lends itself to the production of inexpensive nitrogen-containing iron-chromium alloys of desired nitrogen content, which content may be controlled within desired commercial limits.

As many possible embodiments may be made of our invention, and as many changes may be made in the embodiments hereinbefore set forth, it will be understood that all matter described herein is to be interpreted as illustrative and not in a limiting sense.

We claim:

1. In the production of lump ferrochromium containing nitrogen distributed thruout the same, the art which includes heating low-carbon ferrochromium containing about 70% chromium and the remainder substantially all iron in the form

of crushed lumps of about one-inch size to the critical temperature of 1700° F. to 2400° F. in contact with a nitrogen-containing material decomposable at low temperatures to free the nitrogen content thereof, and maintaining said critical temperature for a period of one to six hours to effect nitrogenation thruout the iron-chromium alloy to an average nitrogen content of at least 0.7%.

2. In the production of lump ferrochromium containing nitrogen distributed thruout the same, the art which includes heating an iron-chromium alloy of low carbon content in the form of crushed lumps of about one-inch size and containing about 70% chromium with the remainder substantially all iron to a temperature of about 1700° F. to about 2400° F. in contact with a nitrogen gas for a period of one hour or more to effect nitrogenation thruout the ferrochromium to an average content of 0.7% or more.

3. In the production of lump ferrochromium containing nitrogen distributed thruout the same, the art which includes heating a low-carbon ferro-alloy in the form of crushed lumps of about one-inch size and containing about 70% chromium with the remainder substantially all iron to a temperature of about 1700° F. to about 2400° F. in contact with calcium cyanamide for a period of one to six hours to effect nitrogenation thruout the ferrochromium to an average content of 1.3% or more.

4. A pre-alloy for introducing nitrogen in producing high-nitrogen stainless steel, comprising an iron-chromium alloy of low carbon content in the form of nitrided lumps of about one-inch size and containing about 70% chromium and having nitrogen distributed thruout the same in the form of nitride needles to an average nitrogen content of 0.7% to 2.0% or more.

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