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[54] **SINTERED, NITROGEN-CONTAINING KEY STEEL**
REFINING ALLOY
9 Claims, No Drawings

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ABSTRACT: A useful method of making key alloys for refining steel by addition to the steel melt whereby alloying elements and nitrogen may be incorporated in the steel, consists of nitriding a nitridable metal or metal alloy, which alloy may be an alloy of two nitridable alloys or a ferroalloy of a nitridable metal, by exposing the metal or alloy to a nitriding atmosphere at an elevated temperature.

SINTERED, NITROGEN-CONTAINING KEY STEEL REFINING ALLOY

By exposing a single metal or metal alloy to the nitriding atmosphere, less than the theoretical amount of nitrogen take-up is achieved. It has been discovered according to the invention that if two or more separate nitridable metals are present, then the nitrogen take-up is unexpectedly improved.

The mixture of nitridable metals may be a mixture of two or more metals, or a metal and an alloy of a different metal, or two or more metal alloys. Such a metal alloy is a ferroalloy.

This invention relates to the production of complex key alloys having a high nitrogen content, for introducing nitrogen into a steel melt.

The introduction of nitrogen into steel can be effected in different ways, the usual method being to use ferroalloys or lime nitrogen, or products containing lime nitrogen. Nitrogen may also be supplied by the addition of organic compounds or by the introduction of nitrogen in gaseous form into the molten steel, although the two latter methods are not of practical importance. Compared with nitrided ferroalloys, lime nitrogen and products containing lime nitrogen have the disadvantage of introducing slag-forming compounds into the steel bath, the 10 to 40 percent nitrogen yield in the steel being somewhat low and subject to major fluctuations. They also create a hazard to operating personnel by forming hydrocyanic acid and cyanide. Thus the use of nitrided ferroalloys is preferred, the nitrogen carriers used being alloys of vanadium, chromium or manganese which possess a high nitriding stability. Ferroalloys that have been melted down, and sintered nitrided ferroalloys are also available for the purpose. As may be expected, in molten alloys the nitrogen distribution is uniform, but compared with sintered alloys their nitrogen content is very much lower. Sintered ferroalloys are therefore more economical to use because of their higher nitrogen content, but they are often rather porous. Consequently they are not easy to submerge in the steel melt and furthermore the resultant nitrogen yields tend to fluctuate.

For nitriding ferroalloys to provide key alloys, several methods are used. Thus the crushed alloy is nitrided under nitrogen gas or gaseous ammonia at temperatures from above 700° C. to below the melting temperature. Since the intake of nitrogen is by diffusion, the alloy that is to be nitrided must be as finegrained as possible. Moreover, in order to complete the nitriding process within a short period of time the temperatures must be as high as possible. For instance, for nitriding manganese and ferromanganese, temperatures between 1,000° and 1,200° C. have been proposed. High temperatures and the required considerable reduction in size are incompatible with economy of production, consequently in practice a compromise is usually made and the nitrogen contents of such alloys are substantially below the theoretically possible levels. For instance with a ferromanganese a nitrogen content of 5 percent is usually considered acceptable, the maximum attainable content being approximately 9 percent nitrogen.

One suggestion for increasing the nitrogen content involves first aluminothermically melting down a manganese-vanadium alloy consisting of industrial vanadic acid and an addition of manganese metal or ferromanganese, the alloy thus obtained being comminuted and nitrided in the solid state. The defect of this method is that a special alloy must first be prepared which, due to the addition of the solid alloying component manganese, is not cheap to produce. Moreover, only alloys within a limited range of vanadium-manganese ratios can thus be obtained.

In another proposal for the preparation of a complex alloy, aluminum is used together with manganese and nitrogen, the purpose of the aluminum being to deoxidize the steel during the alloying process. This ensures a uniform and high acceptance of nitrogen by the steel. Nevertheless it must be considered a disadvantage that a given quantity of aluminum is necessarily introduced into the steel together with the nitrogen, and this is not always desirable.

It is also previously been suggested to nitride ferromanganese or a manganese-chromium alloy in a current of

nitrogen or ammonia gas. For forming a key alloy the resultant sinter product is added to molten ferromanganese or manganese metal. Since this procedure likewise involves two stages it is not economically desirable.

It is the object of the present invention to provide a simple and economic method of producing a dense sintered key alloy having a very high content of nitrogen, which is evenly distributed by performing a heat treatment in a nitriding atmosphere at temperatures exceeding 800° C. Furthermore these advantages are obtained without the necessity of providing the raw materials with a finer grain size or of submitting them to higher nitriding temperatures than have been hitherto conventionally used.

According to the invention these objects are achieved by adding to a ferroalloy, or an alloying metal that is to be nitrided in the solid state, one or more additional metals and/or different ferroalloys.

By the process of the invention, the nitriding of a comminuted ferroalloy at temperatures above 900° C. proceeds at a much faster rate when the second ferroalloy or alloying metal has been added in quantities of at least 10 percent to the alloy that is to be nitrided.

In its broadest terms, the invention is defined as a method of producing sintered, nitrogen-containing key steel refining alloys, comprising nitriding in the solid state at a temperature above 800° C. in a nitriding atmosphere a mixture of at least two substances selected from the class consisting of nitridable metals and nitridable metal alloys, in which mixture at least two different kinds of nitridable metal molecules are separately present.

By the term "nitridable metals" is meant metals which are conventionably nitrided to form key alloys, and thus exclude iron.

Advantages obtained by the process of the invention are that the nitrogen content that can be diffused into the mixed alloy is between 10 and 30 percent higher than that attainable in ferroalloys or alloying metals that are individually nitrided and subsequently mixed, and the addition of the second ferroalloy reduces the time required for nitriding to achieve a specified nitrogen content below that needed for nitriding the several alloys or alloying metals separately. Furthermore such mixed alloys surprisingly sinter together into much more compact lumps at a given temperature, so that they can therefore be readily immersed in a steel bath and they dissolve quickly to provide a high and uniform nitrogen content to the steel. The method of the invention permits the nitrogen-containing mixed alloys to be readily adapted to any particular requirement. For instance if a mixed alloy with a specified nitrogen content is desired, then the nitrogen content can be exactly adjusted by appropriately selecting and correspondingly mixing together the individual alloys. Conversely mixed alloys can be prepared and nitrided which contain the proportions of alloying components the steelmaker desires. In such an instance the nitrogen content of the nitrided mixed alloy is again higher than that which would be achieved if the individually nitrided metals or ferroalloys had been subsequently mixed.

The preparation of the nitrogen-containing mixed alloys can be accomplished in conventional furnaces. The ferroalloys and/or metals are first mixed to the user's specification. Size reduction may be performed by any known method, such as for example grinding, granulating and spraying.

Nitriding is carried out using nitrogen containing gases and/or gaseous ammonia at temperatures between 800° and 1,400° C., preferably between 900° and 1,100° C. The sinter products obtained may then be broken down into lumps of the desired size.

Examples of nitrogen-containing mixed alloys are hereinafter described, using the following ferroalloys:

Ferromanganese, superrefined of grain size 0.3 mm., containing
90.0% Mn
0.1% C
0.03% N

Ferrovanadium, of grain size 0.6 mm., containing

80.2% V
0.05% C
0.013% N

Ferrochrome, superrefined of grain size 0.3 mm., containing
72.0% Cr
0.1% C
0.4% Si
0.03% N

Ferroniobium, of grain size 0.3 mm., containing 65.26% Nb
0.32% Ta
0.04% C
0.002% N

The nitriding operation was performed at 950° C. for a period of 8 hours in a nitrogen atmosphere of 760 torr.

Example 1

The following quantities of alloys were nitrided:

- a. 120 kg. of ferromanganese alone,
- b. 150 kg. of ferrovanadium alone,
- c. 70 kg. of ferromanganese mixed with 140 kg. of ferrovanadium.

The following quantities by weight were obtained:

- a. 130 kg. of ferromanganese, nitrided, containing 83.8% Mn
7.1% N
- b. 168 kg. of ferrovanadium, nitrided, containing 71.5% V
10.5% N
- c. 237 kg. of ferromanganese-ferrovanadium mixture, nitrided, containing 47.2% V
27.0% Mn
10.5% N

If the individually nitrided alloys ferromanganese and ferrovanadium had been mixed in the proportion of 1:2 the calculated nitrogen content of the mixture would have been 9.4 percent nitrogen. However, the nitrided mixture alloy actually contained 10.5% N.

Example 2

The following alloys were nitrided:

- a. 270 kg. of ferromanganese alone
- b. 300 kg. of ferrovanadium alone
- c. 150 kg. of ferromanganese mixed with 150 kg. ferrovanadium in the proportion of ferromanganese to ferrovanadium of 1:1.

The following weights of nitrided product were obtained:

- a. 294 kg. of ferromanganese, nitrided, containing 83.2% Mn
7.7% N
- b. 339 kg. of ferrovanadium, nitrided, containing 71.3% V
11.0% N
- c. 340 kg. of ferromanganese-ferrovanadium mixture, nitrided, containing 35.6% V
40.3% Mn
11.1% N

A mixture in the proportion of 1:1 of the individually nitrided alloys ferromanganese and ferrovanadium would have contained 9.4% nitrogen compared with 11.1% in the nitrided mixture.

Example 3

The following alloys were nitrided:

- a. 200 kg. of ferromanganese, alone
- b. 200 kg. of ferrochrome, alone
- c. 140 kg. of ferromanganese mixed with 70 kg. of ferrochrome; proportion of ferromanganese to ferrochrome =2:1.

The weights of nitrided products obtained were:

- a. 216 kg. of ferromanganese, nitrided, containing 83.55% Mn
7.6% N
- b. 215 kg. of ferrochrome, nitrided, containing 67.1% Cr
6.7% N

- c. 234 kg. of ferromanganese-ferrochrome mixture, nitrided, containing 54.0% Mn
21.8% percent Cr
9.2% N

A mixture of the individually nitrided alloys in the proportion of ferromanganese to ferrochrome of 2:1 would therefore contain only 7.3% nitrogen, whereas the nitrided mixture contains 9.2% nitrogen.

Example 4

The following alloys were nitrided:

- a. 250 of ferrovanadium alone,
- b. 250 kg. of ferrochrome alone,
- c. 140 kg. of ferrovanadium mixed with 70 kg. of ferrochrome, proportion of ferrovanadium to ferrochrome 2:1.

The following nitrided products were obtained:

- a. 279 kg. of ferrovanadium, nitrided, containing 70.5% percent V
10.9% N
- b. 269 kg. of ferrochrome, nitrided, containing 66.5% Cr
6.4% N
- c. 238 kg. of ferrovanadium-ferrochrome mixture, nitrided, containing 47.6% V
20.7% Cr
10.5% N

A mixture of the individually nitrided alloys in the proportion ferrovanadium : ferrochrome =2:1 would have provided 9.4% nitrogen, whereas the nitrided mixture contained 10.5% nitrogen.

Example 5

The following alloys were nitrided:

- a. 150 kg. of ferromanganese alone,
- b. 150 kg. of ferroniobium alone,
- c. 120 kg. of ferromanganese mixed with 30 kg. of ferroniobium: proportion of ferromanganese to ferroniobium =4:1.

The following nitrided quantities were obtained:

- a. 163 kg. of ferromanganese, nitrided, containing 83.2% Mn
7.3% N
- b. 155 kg. of ferroniobium, nitrided, containing 62.9% Nb
3.4% N
- c. 160 kg. of ferromanganese-ferroniobium mixture, nitrided, containing 68.3% Mn
12.45% Nb
7.0% N

By mixing the individually nitrided alloys ferromanganese and ferroniobium in the proportion of 4:1 the average nitrogen content obtained would have been 6.5% compared with 7.0% nitrogen in the nitrided mixture.

In all the above examples the nitrided mixed alloys are superior in mechanical strength to the similarly nitrided individual alloys. Whereas in the case of the individual alloys the apparent density of the nitrided sinter was only 50 to 65% of the true density, the corresponding figures for the mixed alloys were between 60 and 75% of the true density.

According to the invention ferroalloys, for example those used in the above examples, may be replaced by a metal and it is also possible to add one or more metals to the mixture that is to be nitrided. In the method according to the invention the essence of the matter is to use a mixture which contains the alloying metal essential for treating the steel in mixture with another metal, and alloys may also be used. The most convenient procedure is to use ferroalloys both for the basic component of the mixture that is to be nitrided and for the admixture. Generally speaking the alloys may be used in the usual compositions in which they are available on the market. This makes the proposed method particularly economical, since it requires no specially prepared products as raw materials.

Specific examples of mixtures which may be nitrided according to the process of the invention include the following:

Mixtures of manganese metal or ferromanganese, and ferrovanadium, in which the weight ratio of the former to the latter component is preferably between 3:1 and 1:1.

Mixtures of manganese metal or ferromanganese, and chromium metal or ferrochromium, in which the weight ratio of the former to the latter component is preferably between 3:1 and 1:2.

Mixtures of ferrovanadium, and chromium metal or ferrochromium, in which the weight ratio of the former to the latter component is preferably between 2:1 and 1:3.

Mixtures of manganese metal or ferromanganese, and ferroniobium, in which the weight ratio of the former to the latter component is preferably between 4:1 and 1:1.

What is claimed is:

1. A method of producing a sintered, nitrogen-containing key steel refining alloy comprising the steps of:
 - a. selecting at least one nitridable metal selected from the class consisting of manganese, vanadium, chromium, niobium and ferroalloys thereof;
 - b. selecting at least one nitridable metal different from the metal selected in step (a) and selected from the class consisting of manganese, vanadium, chromium, niobium and ferroalloys thereof;
 - c. crushing the metal of step (a) to form a powder;
 - d. crushing the metal of step (b) to form a powder;
 - e. physically mixing the crushed metals of steps (c) and (d) such that the molecules of at least two separate and different kinds of said nitridable metal molecules are present in a proportion such that metal selected in step (b) is present in an amount of at least 10 percent, the balance being the metal selected in step (a);
 - f. nitriding the mixture of crushed metals of step (e) in a nitriding atmosphere at a temperature above 800° C.,

thereby producing a sintered, nitrogen-containing key steel refining alloy.

2. A method according to claim 1, in which the said mixture is a mixture of a manganese substance selected from the class consisting of manganese and ferromanganese, and ferrovanadium.

3. A method according to claim 2, in which the ratio by weight of manganese substance to ferrovanadium is between 3:1 and 1:1.

4. A method according to claim 1, in which the said mixture is a mixture of a manganese substance selected from the class consisting of manganese and ferromanganese, and a chromium substance selected from the class consisting of chromium and ferrochromium.

5. A method according to claim 4, in which the ratio by weight of manganese substance to chromium substance is between 3:1 and 1:2.

6. A method according to claim 1, in which the said mixture is a mixture of ferrovanadium and a chromium substance selected from the class consisting of chromium and ferrochromium.

7. A method according to claim 6, in which the ratio by weight of ferrovanadium to chromium substance is between 2:1 and 1:3.

8. A method according to claim 1, in which the said mixture is a mixture of a manganese substance selected from the class consisting of manganese and ferromanganese, and ferroniobium.

9. A method according to claim 8, in which the ratio by weight of manganese substance to ferroniobium is between 4:1 and 1:1.

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