METHOD FOR MANUFACTURING NITRIDE-CONTAINING LOW-CARBON STRUCTURAL STEELS

FIG. 1

FIG. 2

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BY

NOTICE TO ATTORNEYS
METHOD FOR MANUFACTURING NITRIDE-CONTAINING LOW-CARBON STRUCTURAL STEELS

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Filed Feb. 21, 1966, Ser. No. 529,013

Claims priority, application Japan, Feb. 25, 1965,

40,10,837

U.S. Cl. 148—12

Int. Cl. C21c 1/28, 1/22; C21d 7/14

ABSTRACT OF THE DISCLOSURE

Method for manufacturing nitride-containing low carbon structural steel with carbon up to 0.25%, total nitrogen at least 0.012% of which at least 0.010% is present as nitride, either of aluminum alone or in combination with nitrides of one or more other elements, the method comprising (1) heating the steel to at least 1,300 °C, (2) during cooling from said temperature, passing the temperature range of 1,250 °C to 1,050 °C in at least ten minutes, (3) in further cooling passing the range of 750 °C to 600 °C in at least ten minutes or holding at any temperature within that range for at least ten minutes, (4) reheating the steel with or without cooling down to room temperature, and (5) heat treating the steel at a temperature above the A3 transformation point. The steel so produced has improved mechanical properties, particularly low temperature toughness.

This invention relates to an improved method for manufacturing nitride-containing low-carbon structural steels. More particularly, this invention relates to an improved method for manufacturing nitride-containing low-carbon structural steels, the steel containing, by check analysis, carbon up to 0.25%, total nitrogen at least 0.012%, of which at least 0.010% is nitride nitrogen, the nitride being either that of aluminum, or of any one or more of the elements beryllium, columbium, vanadium, titanium or zirconium, the balance or the free uncombined nitrogen being less than 0.003%, the method comprises, (1) heating the steel to at least 1,300 °C, (2) in the course of cooling from said temperature, either passing the temperature range of 1,250 °C to 1,050 °C in at the most ten minutes or at a mean cooling rate of at least 20 °C/min., and (3) in the course of cooling further, either passing the temperature range of 750 °C to 600 °C in at least ten minutes or at a mean cooling rate of at least 15 °C/min., or holding at any temperature within said temperature range for at least ten minutes, (4) reheating the steel without cooling it to room temperatures, and (5) heat treating the steel at a temperature above the A3 transformation point. The rate of cooling or heating at temperatures outside the specified ranges can be as desired.

The primary purpose of this invention resides in the improvement of a manufacturing method for high quality steels that are economical in thermal expenditure than other known methods, and yet is one that can be practised or adapted readily in or to the current steelmaking processes as it requires no additional equipment.

The second purpose of this invention resides in the provision of inexpensive structural steels of improved mechanical properties, particularly the low temperature toughness.

Other purposes of this invention will in part be explained and in part be understood from the following description.

In the disclosure of this inventive method, reference will be made to the accompanying drawings, where FIG. 1 is a schematic diagram (not to scale) to show the first embodiment of the process of this invention, FIG. 2 is a similar diagram for the second embodiment of the process, and FIG. 3 shows the precipitation behavior of aluminum nitride in isothermal heating treatment (curve A) and isothermal cooling treatment (curve B). In this specification, all the chemical analyses are given in terms of weight percent and the temperature in centigrade.

This method of the invention comprises two major embodiments. The first embodiment applies to steels of such nature that the content and kind of the alloying element or elements, other than but with due consideration to the carbon, nitrogen and nitride-former or formers, make the steel to finish in the ferrite-pearlite double phase structure upon normalization treatment, namely when heated to a temperature above the A3 transformation point and cooled in air. This kind of steel will be referred to as the first kind steel hereinafter.

The second embodiment applies to steels of such nature that the content and kind of the alloying element or elements, other than but with due consideration to the carbon, nitrogen and nitride-former or formers, make the steel to finish in the martensite or bainite structure upon quenching treatment, namely when heated to a temperature above the A3 transformation point and quenched. This kind of steel will be referred to as the second kind steel hereinafter.

The principal five-step process of the method of this invention lends itself to the first or the second kind of steel as follows. In the first embodiment of the process, the first kind steel is (1) heated to at least 1,300 °C, (2) in the course of cooling therefrom, either cooled through the temperature range of 1,250 °C to 1,050 °C in at the most ten minutes or at a mean cooling rate of at least 20 °C/min., working the steel if so desired, (3) in the course of cooling further, either cooled through the temperature range of 750 °C to 600 °C in at least ten minutes or at a mean cooling rate of at least 15 °C/min., or held at any temperature within said temperature range for at least ten minutes, (4) reheated to the normalization temperature without cooling to room temperatures, and (5) normalized. This embodiment is schematically illustrated in FIG. 1.

In the second embodiment, the second kind steel is (1) heated to at least 1,300 °C, (2) in the course of cooling therefrom, either cooled through the temperature range of 1,250 °C to 1,050 °C in at the most ten minutes or at a mean cooling rate of at least 20 °C/min., working the steel while being cooled, (3) in the course of cooling further, either cooled through the temperature range of 750 °C to 600 °C in at least ten minutes or at a mean cooling rate of at least 15 °C/min., or held at any temperature within said temperature range for at least ten minutes, (4) reheated to the quenching temperature without cooling to room temperatures, and (5) quenched or quench-and-tempered. This embodiment process is schematically illustrated in FIG. 2.

The mechanical properties, particularly the low temperature notch toughness of the steel, can be improved further by repeating the steps (3) to (5) of either embodiment two or more times.

As will be seen, the step (5) of either embodiment which differentiates the two, namely essentially the normalization treatment in the first, and essentially the quenching or quench-and-tempering treatment in the second. The other difference resides in step (2), where a hot working is required for the second embodiment, whereas it is not mandatory for the first. Those differences are attributed to the difference in amount and kind of alloying element or elements other than carbon, nitrogen and nitride-forming.
components, the latter being common to the steels of the first and the second kind. Of several known methods for manufacturing or heat treating steels that contain less than 0.016% nitrogen and more than 0.016% nitride nitrogen, the nitride being principally the aluminum nitride, two are representative and of particular interest. In one, the steel that is semi-finished through ordinary procedures, including soaking, blooming and slab rolling, is heated to a temperature in the $A_3$ to 1,100° range, rapidly cooled to room temperature then tempered at a temperature between 150° and the $A_1$ transformation point. This will be referred to as the known quench-and-tempering method hereinafter.

In the other, the steel is solution treated with regard to aluminum nitride, namely, heated to a temperature that is determined by the contents of nitrogen and aluminum so as to completely dissolve the aluminum nitride precipitates, rapidly cooled to 1,000° at a rate of at least 90°/min., heated to a temperature between the $A_3$ and 950°, whereafter the normalization is once or more times repeated. This method will be referred to as the known normalization method hereinafter.

All the known methods, the two aforementioned in particular, were based on an observation that the precipitation of aluminum nitride is most enhanced in the temperature range of approximately 850° to 1,100° as shown by the curve A of Fig. 3. Thus, in all the methods hitherto proposed, the precipitation of aluminum nitride with that of heat treatment for ordinary steels is taken advantage of. Here, the precipitation of aluminum nitride is conceived to take place from the gamma-iron or austenite matrix of the steel.

However, after extensive research and experiments, it has now been found rather unexpectedly that when the steel is cooled from the solution treatment temperature down to the designated temperature and held therefor for precipitation treatment (the isothermal cooling treatment), as opposed to its being heated up from room temperature to the same after once having been solution treated and rapidly cooled so as to conserve the decomposition of aluminum and nitrogen (the isothermal heating treatment), by which curve A of Fig. 3 was determined, the precipitation behavior of aluminum nitride is markedly and totally different. This is shown by curve B in Fig. 3. As may be seen, there are now two fairly sharp precipitation peaks as against the one and single broad peak of curve A. It will further be noticed that one of the peaks is located at the 1,250° to 1,050° range, namely in the gamma-iron range, while the other is at the 750° to 600° range, namely in the alpha-iron or ferrite range. It was found empirically, furthermore, that the rate of precipitation is far greater at the latter peak range than it is at the former, and that the aluminum nitride particles that precipitate in the latter range contribute more to the improvement of low temperature toughness of the steel than those obtained in the former.

Thus, this invention is based on the three newly made discoveries described above. Namely, the first point in this invention is to have aluminum nitride precipitate in the temperature range of 750° to 600°, or from the ferrite matrix. In both embodiments of the process, this is achieved in step (3). The second point is to suppress the precipitation of aluminum nitride, or to allow as little precipitation as possible while the steel is still austenitic. In this consideration, the solution treatment temperature and the cooling rate through the 1,250° to 1,050° range is critical, as specified in the steps (1) and (2). Here, it is natural that the higher the aluminum and nitrogen contents, the higher the solution temperature should be chosen, but a complete dissolution of aluminum nitride as demanded in the known normalization method is not mandatory though desirable. It is natural again that the faster the cooling rate from the solution temperature, the better suppressed is the precipitation of aluminum nitride, but a rate as fast or faster than 90°/min. is demanded in the known normalization method.

The third point is to recrystallize the steel into the finer granular structure, in which the aluminum nitride particles already precipitated in the 750° to 600° range act as effective nuclei. A finer grain size structure can be obtained when said recrystallization is done by transformation, namely by normalization or quenching treatment. This is step (5).

The fourth point relates to the hot working that is to be performed concurrently with step (2), which is mandatory for the second kind of steels. The degree or extent of said hot working should be determined for each steel and each deformation practice, but in the case of flat rolling, a reduction in thickness of at least 20% is necessary.

The fifth point is to reheat the steel, once it has been cooled through the 750° to 600° range, up to the subsequent heat treatment temperature without letting it cool to room temperatures. This is step (4), by which a great quantity of heat is conserved to contribute to the improvement of heat economy. Also, the entire manufacturing procedure is much simplified and the production cost is reduced. Should the heat economy be disregarded in favor of other considerations, such as, for example, of production convenience, the steel may be allowed to cool through to room temperatures without affecting the quality of the product steel, provided other points are satisfied.

With regard to the nature of the steel, at least three points must be observed. One is the content of free nitrogen, or that part of the total nitrogen which is left uncombined into nitride but dissolved in the steel matrix, which should be kept to less than 0.003% by check, or product, analysis. As is known, the more free nitrogen is present, the more susceptible becomes the steel to embrittlement, but no noticeable harm is observed when it is held to this range.

The second point is the choice and prescription of nitride-forming metallic element with respect to the nitrogen content. For example, aluminum of approximately 1.93 times the nitrogen should be theoretically sufficient to convert all the nitrogen into nitride. In practicing this invention, at least approximately 2.5 times of aluminum with reference to the nitrogen content is necessary to bring the free nitrogen to the aforesaid un-harmful level. Although this can be done the easier the more aluminum is provided, yet the free metallic aluminum, or that part of said soluble aluminum which is not combined with nitrogen and dissolved in the steel matrix as solid solution, should better be kept to less than 0.10%, for such aluminum tends to stimulate the grain growth and as a consequence affects the mechanical properties of the steel adversely.

This shortcoming associated with aluminum can be overcome by providing another nitride-former in addition to aluminum. For this purpose, any one or more of the elements beryllium, columbium, vanadium, titanium and zirconium, particularly the first three, are suited. The precipitation temperature ranges of the nitrides of the first three are conveniently coincident with that of steps (4) and (5) in order to do an effective elimination of the free nitrogen off the matrix. Also, the precipitated particles of those three are known to contribute to the improvement of low temperature toughness of the steel.

Table 1 gives the chemical composition of steels by check analysis, the balance being substantially iron with incidental or unavoidable impurities, such as sulphur or phosphorus. In the table, the steels of the L series are the first kind, those of the H series the second, while the K series relate to commercial steels of such nature as to
be classed with either the first or the second kind but for the shortage in the nitrogen content.

Table 2 summarizes the mechanical properties of the steels as produced by this invention. In the table, εv<sub>2</sub>, εv<sub>5</sub>, εv<sub>15</sub>, εv<sub>30</sub> and εv<sub>60</sub> are the characteristic values in the 2 mm. V-notch Charpy testing, denoting, respectively, the notch impact strength at 0°, the transition temperatures of 15 ft.-lb. basis, of 30 ft.-lb. basis, and of 50% shear fracture appearance basis.

**Example 1**

The steel L-1 of Table 1 was (1) heated to 1,350°, (2) cooled through the 1,270°–1,000° range in eight minutes, no hot working, (3) held for fifteen minutes at 700°, (4) reheated therefrom, and (5) held for thirty minutes at 930° and cooled in air. The mechanical properties of the so made steel are shown in Table 2 as L-1-A.

**Example 2**

The steel L-1 of Table 1 was (1) heated to 1,330°, (2) hot rolled starting at 1,270° and finishing at 1,000°, giving a reduction in thickness of 30% while being cooled through the same temperature range in three minutes, the rest the same as in Example 1. This steel is shown in Table 2 as L-1-B.

**Example 3**

The steel L-2 of Table 1 was (1) heated to 1,330°, (2) cooled through the 1,300–1,000° range at a mean cooling rate of 50°/min., no hot working, (3) cooled through the 750°–600° range at a mean cooling rate of 10°/min., (4) reheating from 550°, and (5) the same as in Example 1. This is the steel L-2-A in Table 2.

**Example 4**

The steel H-1 of Table 1 was (1) heated to 1,350°, (2) rolled starting at 1,350° and finishing at 1,050°, giving a reduction in thickness of 45% while being cooled in ten minutes, (3) and (4) the same as in the Example 3, and (5) held for thirty minutes at 930°, quenched in water, and held for one hour at 630°–660°, and cooled in air. This is the steel H-1-A in Table 2.

**Example 5**

The steel H-2 of Table 1 was (1) heated to 1,350°, (2) rolled similarly as in the Example 4, except for the reduction in thickness which was 52%, (3) held for thirty minutes at 700°, (4) reheated therefrom, and (5) the same as in the Example 4. This is the steel H-2-A in Table 2.

**Example 6**

The steel H-3 of Table 1 was (1) heated to 1,330°, (2) rolled starting at 1,275° and finishing at 1,010°, giving a reduction in thickness of 36% while being cooled at a mean cooling rate of 65°/min., the rest the same as in the Example 5. This is the steel H-3-A in Table 2.

**Example 7**

The steel H-3 of Table 1 was (1) heated to 1,350°, (2) rolled starting at 1,350° and finishing at 1,100°, giving a reduction in thickness of 35% while being cooled through the 1,250°–1,050° range at a mean cooling rate of 30°/min., (3) cooled through the 750°–600° range in twenty minutes, (4) reheating from 600°, and (5) the same as in Example 4. This is the steel H-3-B in Table 2.

**Example 8**

The steel K-1 of Table 1 was (1) heated to 1,350°, (2) cooled through the 1,270°–1,000° range in eight minutes, no working, (3) held for fifteen minutes at 700°, (4) reheated therefrom, and (5) held for thirty minutes at 930° and cooled in air.

This is the identical treatment as that of Example 1, in that it is the first embodiment of this invention as applied to an improperly compositioned steel. This steel is shown as K-1-A in Table 2.

**Example 9**

The steel K-2 of Table 1 was (1) heated to 1,350°, (2) rolled starting at 1,350° and finishing at 1,050°, giving a reduction in thickness of 45% while being cooled through in ten minutes, (3) and (4) the same as in Example 3, and (5) held for thirty minutes at 930°, quenched in water, held for one hour in the 630°–660° range, and cooled in air.

This is the identical treatment as that in the Example 4, in that it is the second embodiment of this invention as applied to an improperly compositioned steel. This steel is shown as K-2-A in Table 2.

By the seven steels of Tables 1 and 2, comprising the steels L-1-A to H-3-B, it will be observed that the method of this invention produces steels of unusual mechanical properties, low temperature notch toughness, in particular. It will further be noted that the method develops its potentiality best for steels of proper composition as set forth, while the commercial steels K-1 and K-2 are low in nitrogen content and consequently the effect of this method is not satisfactorily developed.

This can be seen by comparing the steel K-1-A with L-1-A or the steel K-2-A with L-1-A. It will be seen that the steel K-2-A contains as much as 0.007% nitrogen, and therefore an appreciable quantity of aluminum nitride was duly precipitated by the method of the invention, a fact which is attested to by the noticeably improved εv<sub>2</sub> value. However, the deficiency of nitrogen or aluminum nitride precipitate is reflected on the transition temperatures, which are markedly inferior to those of the steel H-1-A, the properly compositioned steel which contains nitrogen by 0.013%.

**Example 10**

The steel H-1 of Table 1 was (a) heated to 1,350°, (b) rolled starting at 1,350° and finishing at 1,050°, giving a reduction in thickness of 45% while being cooled through in ten minutes, (c) allowed to cool to room temperature, (d) upon reheating to 930°, heated through the 600°–750° range in fifteen minutes, or at a mean heating rate of 10°/min., and (e) held for thirty minutes at 930°, quenched in water, tempered in the 630°–660° range, and cooled in air. This steel is shown as H-1-B in Table 2.

It will be noted that in this example, the second embodiment of the process of this invention was generally followed except the deviations in the steps (c) and (d), which make this example confirm apparently to the known quench-and-tempering method. As this is the severer heat treatment than the principal method of the invention, the produced steel, the H-1-B, is slightly superior to its counterpart, the H-1-A of Example 5, in the mechanical properties.

It is to be understood, however, that the process of the last example has in common with the method of this invention that the precipitation of aluminum nitride is so designed as to take place in the 600°–750° range, namely from the ferrite matrix. Here, the similarity of curve A with curve B, both in FIG. 3, in the temperature range from room temperatures up to approximately 700° is utilized. Therefore, other points being similar to this invention, this example should be regarded as a modification thereof, in that it is one way to obtain better steels at an expense of the heat economy.

**REFERENCES**

British patent specification, 808,556, Feb. 4, 1959.
TABLE 1.—CHEMICAL COMPOSITION (WT. PERCENT)

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Total N</th>
<th>Sol. Al</th>
<th>Free N</th>
<th>Others</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-1</td>
<td>0.11</td>
<td>0.35</td>
<td>0.27</td>
<td>0.08</td>
<td>0.02</td>
<td>0.02</td>
<td>0.023</td>
<td>0.095</td>
<td>0.003</td>
<td></td>
<td></td>
<td>First kind.</td>
</tr>
<tr>
<td>L-2</td>
<td>0.14</td>
<td>0.37</td>
<td>0.26</td>
<td>0.09</td>
<td>0.02</td>
<td>0.03</td>
<td>0.016</td>
<td>0.018</td>
<td>0.005</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
<tr>
<td>L-3</td>
<td>0.16</td>
<td>0.22</td>
<td>0.32</td>
<td>0.10</td>
<td>0.01</td>
<td>0.01</td>
<td>0.013</td>
<td>0.007</td>
<td>0.003</td>
<td></td>
<td></td>
<td>Second kind.</td>
</tr>
<tr>
<td>L-4</td>
<td>0.17</td>
<td>0.30</td>
<td>0.28</td>
<td>0.10</td>
<td>0.02</td>
<td>0.02</td>
<td>0.030</td>
<td>0.133</td>
<td>0.001</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
<tr>
<td>K-1</td>
<td>0.14</td>
<td>0.24</td>
<td>0.26</td>
<td>0.05</td>
<td>0.06</td>
<td>0.07</td>
<td>0.019</td>
<td>0.058</td>
<td>0.001</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
<tr>
<td>K-2</td>
<td>0.14</td>
<td>0.27</td>
<td>0.30</td>
<td>0.08</td>
<td>0.01</td>
<td>0.08</td>
<td>0.004</td>
<td>0.015</td>
<td>0.002</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
</tbody>
</table>

1 Sol. Al stands for solid soluble aluminum.

TABLE 2.—MECHANICAL PROPERTIES (PLATE THICKNESS, 25 MM.)

<table>
<thead>
<tr>
<th>Steel</th>
<th>Yield strength, kg/m.m.²</th>
<th>Elongation, percent</th>
<th>v&lt;sub&gt;E&lt;/sub&gt;O, kg/m/cm.²</th>
<th>v&lt;sub&gt;T&lt;/sub&gt;150 ° C.</th>
<th>v&lt;sub&gt;T&lt;/sub&gt;200 ° C.</th>
<th>v&lt;sub&gt;T&lt;/sub&gt;250 ° C.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-1-A</td>
<td>24.5</td>
<td>44.7</td>
<td>41.3</td>
<td>20.2</td>
<td>-77</td>
<td>-88</td>
<td>Example 1</td>
</tr>
<tr>
<td>L-2-B</td>
<td>25.2</td>
<td>45.1</td>
<td>41.1</td>
<td>20.0</td>
<td>-71</td>
<td>-71</td>
<td>Example 2</td>
</tr>
<tr>
<td>M-1-A</td>
<td>25.0</td>
<td>44.5</td>
<td>41.1</td>
<td>20.5</td>
<td>-70</td>
<td>-70</td>
<td>Example 3</td>
</tr>
<tr>
<td>H-2-A</td>
<td>24.9</td>
<td>44.6</td>
<td>41.4</td>
<td>21.5</td>
<td>-105</td>
<td>-90</td>
<td>Example 4</td>
</tr>
<tr>
<td>H-2-A</td>
<td>24.8</td>
<td>45.2</td>
<td>42.3</td>
<td>23.3</td>
<td>-111</td>
<td>-104</td>
<td>Example 5</td>
</tr>
<tr>
<td>K-1-A</td>
<td>26.5</td>
<td>45.9</td>
<td>41.0</td>
<td>18.5</td>
<td>-84</td>
<td>-71</td>
<td>Example 6</td>
</tr>
<tr>
<td>K-2-A</td>
<td>27.2</td>
<td>46.0</td>
<td>41.3</td>
<td>18.0</td>
<td>-99</td>
<td>-99</td>
<td>Example 7</td>
</tr>
<tr>
<td>K-2-B</td>
<td>27.0</td>
<td>46.0</td>
<td>41.7</td>
<td>19.5</td>
<td>-89</td>
<td>-89</td>
<td>Example 8</td>
</tr>
</tbody>
</table>

What I claim is:

1. Improved method for manufacturing nitride-containing low-carbon structural steels according to any one of foregoing claims 1, 2, 3 or 4 in which the steps (2) to (5) are repeated two or more times.

2. The improved method for manufacturing nitride-containing low-carbon structural steels according to claim 1, in which the step (3) is essentially the quenching or quench-and-tempering treatment.

3. The improved method for manufacturing nitride-containing low-carbon structural steels according to claim 1 or 2, in which the step (5) is essentially the normalizing treatment.

4. The improved method for manufacturing nitride-containing low-carbon structural steels according to claim 1 or 2, in which the step (5) is essentially the quenching or quench-and-tempering treatment.

5. Improved method for manufacturing nitride-containing low-carbon structural steels according to any one of foregoing claims 1, 2, 3 or 4 in which the steps (3) to (5) are repeated two or more times.

6. Improved method for manufacturing nitride-containing low-carbon structural steels as defined in claim 1 in which the steel is (1) heated to at least 1,300 ° C., (2) passing the temperature range of 1,250 ° C. to 1,050 ° C. in at the most ten minutes, (3) cooling the steel to ambient temperatures, (4) in the course of reheating the steel to the heat treatment temperature, holding the temperature range of 700 ° C. to 750 ° C. at least ten minutes and (5) heat treating the steel at a temperature above the A<sub>3</sub> transformation point.

7. The method according to claim 1 which comprises effecting in step (3) further cooling by passing the steel through the temperature range of 750 ° C. to 600 ° C. in at least ten minutes.

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