

UNITED STATES PATENT OFFICE

2,410,322

TREATMENT OF MANGANESE STEEL

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No Drawing. Application September 28, 1943,
Serial No. 504,146

7 Claims. (Cl. 134-3)

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The invention relates to the treatment of manganese steel, and more particularly to the treatment of high manganese, high carbon steel to eliminate surface brittleness, to increase its ductility, and to improve its appearance and surface characteristics; and this application is a continuation in part of and sets forth certain improvements upon the inventions of our prior application entitled Treatment of manganese steel, filed May 18, 1942, Serial No. 443,452, which has matured into Patent No. 2,368,955, dated Feb. 6, 1945.

Some of the difficulties which have been encountered in the manufacture of cold rolled sheets and strips of the thinner gauges from high manganese, high carbon steel in order to provide material that is soft, ductile and has deep drawing qualities for the manufacture of helmets, are set forth in said prior application.

These difficulties arise because high manganese steel work hardens very quickly and can ordinarily be cold rolled to a maximum of only about 25 per cent reduction; and heat treatment is then required to soften the same and enable further cold rolling. A number of cold rolling operations must be performed in order to reduce the thickness of the thinnest available hot rolled high manganese, high carbon steel having a nominal gauge of .109 inch to a cold rolled sheet or strip as thin as .044 to .033 inch.

The heat treatment necessary to soften the steel and restore ductility following a cold rolling operation, frequently oxidizes and decarburizes the surface layers of the steel and many bad or damaging conditions result from such oxidation and decarburization.

Thus, it is pointed out in said prior application that when "Hadfield" steel is decarburized it is unable to completely retain austenite at room temperatures, and on cooling, all or part of the austenite apparently decomposes and forms epsilon iron or alpha iron, or both, in varying proportions; and that these decarburized surface layers containing epsilon iron or alpha iron or both are brittle and may be formed with a myriad of small cracks which develop and increase in size giving a characteristic granulated or frosty appearance when the material is subjected to deep drawing operations.

Because of these difficulties, a considerable quantity of high manganese steel has been damaged in the manufacture of thin gauge, cold rolled, high manganese steel and is in a form that may be termed as scrap. However, such scrap material is very valuable because of the inherent

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high value of the material itself, and because of the ever present critical condition of scrap. The reclamation or salvaging of such damaged material therefore involves a tremendous saving of both money and material and a contribution to the conservation of critical materials.

Said prior application and the present improvements thereon are both directed to methods of treating cold rolled, high manganese strip steel and the like, which has been damaged during heat treatment thereof by decarburization and oxidation, so as to reclaim the material and provide a finished product in which the brittle surface layers have been eliminated or removed, leaving manganese steel which is substantially entirely austenitic in character having great hardness, toughness and wearing power combined with much ductility.

In said prior application we have pointed out that cold rolled, heat treated, high manganese steel strips, sheets and the like may be treated in a dilute solution of nitric acid, approximately up to 5% nitric acid by weight in water, at a temperature of 140° to 200° F. for from one to approximately six minutes depending upon the amount of surface metal to be removed and upon the concentration and temperature conditions, for removing the scale formed during previous heat treatment, and for removing the undesirable decarburized metal surface layers which are extremely detrimental to strength and ductility; so as to provide a cold rolled, high manganese, strip or sheet steel product having a bright, lustrous, relatively smooth, pebbled surface, free of brittleness and having high ductility.

In said prior application it is further pointed out that after the metal has been subjected to the acid attack, a thin brown sludge or precipitate may remain on the surface, which may be removed by scrubbing; or if the sludge or precipitate is tenacious it may be loosened by passing the strip through a dilute solution of sulphuric acid or hydrochloric acid in water, or through any other usual cleaning solution, prior to the scrubbing operation.

We have discovered, however, that in some instances the thin brown sludge or precipitate is very tenacious and the removal of the same has been very difficult and is quite a problem.

The present invention is directed particularly to the latter problem and constitutes a modification of or improvement upon the process set forth in our prior application, which modified process of the present invention greatly eases the problem of removing the sludge which may

form as a result of the nitric acid attack, and which also improves the appearance of the resulting product.

It is therefore an object of the present invention to eliminate or remove the brittle surface layers from cold rolled, heat treated, high manganese steel so as to remove the epsilon or epsilon and alpha iron contained therein and leave manganese steel which is substantially entirely austenitic in character, in order to obtain a product having a bright, lustrous, relatively smooth, pebbled surface, free of brittleness and having high ductility and the normal properties of austenitic manganese steel.

It is a further object of the present invention to provide a method of treating high manganese steel with various acids and alkalies for the removal of scale and brittle surface metal, and also the sludge produced in connection with the removal of such scale and brittle surface metal, without etching or pitting the metal.

It is also an object of the present invention to provide a new treatment of high manganese steel utilizing weak and relatively inexpensive chemicals for scale and brittle surface metal removal and for the production of a product having a bright lustrous, relatively smooth pebbled surface.

Likewise, it is an object of the present invention to provide a new treatment of high manganese steel by which the surface appearance, toughness, strength, ductility and drawing qualities of the steel are improved.

Also, it is an object of the present invention to provide a treatment for reclaiming or salvaging cold rolled, light gauge, high manganese steel, which has been damaged during the heat treatment thereof, which may be carried out quickly and cheaply to provide a perfectly satisfactory and useable light gauge, cold rolled, high manganese strip steel product from material which would ordinarily be classed as scrap.

These and other objects may be obtained, the stated results achieved, and the described difficulties overcome by the methods, steps, products, treatments, and discoveries which comprise the present invention, the nature of which is set forth in the following general statement and a preferred embodiment of which is set forth in the following description, and which are particularly and distinctly pointed out and set forth in the appended claims forming part hereof.

The nature of the present improvements may be stated in general terms as preferably including, in the treatment of high manganese, high carbon steel, which has been heat treated to soften the same and to restore ductility and which has been damaged as a result of such heat treatment by oxidation and surface decarburization and embrittlement, the steps of subjecting the same to the action of a hot bath of a dilute aqueous solution of nitric acid, say up to 5% nitric acid by weight in water, for from 1 to 5 minutes, then washing in hot water to clean away the acid, then washing in a hot solution of sodium or alkali metal hydroxide to soften the sludge which may have formed on the surface, then washing in water to remove the hydroxide solution, then washing in a dilute aqueous solution of hydrochloric acid to further loosen and partially dissolve the sludge, then washing in water and wiping off or removing the loosened sludge, then washing in hot water and drying with hot air, and then preferably oiling the surface to provide a bright, ductile product free of

brittle surface layers, scratches, scale patterns and roughness.

The manufacture of high manganese steel strips will be briefly described in connection with the description of the present improvements.

High manganese, high carbon strip steel of the "Hadfield" type is hot rolled down to the thinnest possible gauge to which it can be rolled without damaging the strip or hot mills, which may be approximately .109 inch in thickness. The strip is then cold rolled to maximum allowable reductions with intervening heat treatment. These cold rolling operations involve approximately 25% reductions for this type of steel; and the austenitizing heat treatment following each cold rolling is such as to dissolve brittle carbides and retain carbon in solution and render the steel as fully austenitic as is possible. The steel is pickled in the usual way for scale removal after each heat treatment. After the desired approximate finished gauge has been obtained by cold rolling and heat treatment, which may be .044 to .033 inch in thickness, the cold rolled heat treated strip steel, if it has been damaged by oxidation, decarburization and surface embrittlement, is then subjected to the special treatment of the present invention.

The special treatment of the present invention may be used for any one of the pickling operations following any cold rolling and heat treating steps, but normally it is unnecessary to do so and ordinarily it will only be used following the last cold rolling step in order to reclaim or salvage material which may have been damaged.

As previously stated, in addition to forming scale, the result of heat treatment utilized after each cold rolling operation, may be to decarburize the surface layers of the steel, which apparently results in the formation of epsilon or alpha iron or both in the surface layers upon quenching.

These undesirable surface layers are removed by passing the strip through and subjecting it to the action of a hot dilute solution of up to about 5% nitric acid by weight in water, for from 1 to 5 minutes, depending upon the amount of metal to be removed. The action of the hot nitric acid bath is most rapid and effective if operated at a temperature of from 180° to 210° F., but this sometimes produces some acid embrittlement, which, however, tends to disappear after several hours or after treatment with steam or hot air.

Accordingly, the preferred temperature of operation of the acid bath is between 180° and 210° F., although this temperature may be reduced somewhat to somewhere within the range of 140° to 200° F. given in our prior application if acid embrittlement difficulties are encountered.

We have discovered further that in some instances, the addition of from 1 to 5% by weight of ammonium nitrate to the nitric acid bath seems to increase the solubility of iron ions and therefore lengthens the useable life of the nitric acid bath solution. The brightness of the finished produce decreases with an increase of iron in solution in the acid, and by increasing the solubility of the iron ions by the ammonium nitrate addition, the solution may be used longer. The solution may be rejuvenated by additions of nitric acid, but after the solution has been used too long, pitting may result and a new solution must be provided. Care must be taken not to reduce the gauge of the material being treated below allowable tolerances.

After the material has been subjected to the acid attack, it is washed in hot water for a few seconds to clean away any acid that may remain on or adhere to the surface of the material being treated.

In cases where the acid attack results in the formation of a brown or black sludge on the surface of the strip, the strip is passed through and subjected to the action of a hot bath of a solution of about 10% sodium, potassium or alkali metal hydroxide by weight in water, maintained at a temperature of about 160° to 180° F. for from 15 to 45 seconds, preferably about 30 seconds, to soften the sludge formed on the surface of the high manganese steel. During this treatment, the sludge seems to swell up, which apparently aids in its ready removal by subsequent treatment.

If the copper content of the steel is high, a thin flash coating of copper may be deposited on the strip during the treatment in the alkali metal hydroxide bath, and this copper coating is not harmful and possibly is beneficial. However, its deposition may be prevented by adding about 1/2 of 1% of sodium or potassium sulphide to the alkali metal hydroxide solution.

The strip is then washed in water to remove the hydroxide solution from the surfaces thereof and is then passed through and subjected to the action of a dilute solution of about 2% hydrochloric acid by weight in water, maintained at a temperature of 140° F. to 180° F. to loosen and partially dissolve the swelled sludge on the surface. The strip is only treated in the hydrochloric acid solution for a few seconds because prolonged treatment tends to dull the surface. We have discovered that the hydrochloric acid solution sludge loosening or dissolving treatment does not operate satisfactorily unless the sludge has been previously treated in the alkali metal hydroxide bath.

The sludge may now be easily removed by washing in water and wiping the sludge off the strip surfaces. A severe scrubbing operation is not necessary, although a light scrubbing may be substituted for wiping if desired.

The strip is then washed with hot water and dried with hot air and finally oiled to provide the finished product having high ductility which is fully austenitic in character with the related characteristics of austenitic high manganese steel fully developed entirely throughout the metal of the strip and with a smooth, bright metal surface finish which is not etched or pitted.

While the process has been described in connection with the manufacture of strip steel or stripsheets, the present invention is also applicable in connection with the manufacture of other high manganese steel products such as sheet steel in accordance with sheet practice, wherein the special treatment is carried out following the final rolling and heat treating operations to remove brittle surface layers and provide a finished product having the same characteristics as those discussed herein in connection with the manufacture of strips.

Accordingly, when the term "strip" is used herein and in the appended claims, the term is intended to include the treatment of hot or cold rolled high manganese steel strips, stripsheets, sheets, plates, bars, rods, wires, forgings or castings and the like, in order to remove brittle surface layers and other surface imperfections.

When the term "strips of the lighter gauges" is used herein and in the appended claims, that

term is intended to include strips, stripsheets, sheets and the like as thin as .044 to .033 inch in thickness, or thinner, and which require for production at least one and usually many more than one cold rolling operation followed by a heat treatment when made of high manganese or "Hadfield" steel.

Finally, when the term "high manganese steel" is referred to herein, it means steels of the "Hadfield" type, which generally contain from 10 to 20% manganese and from 1 to 1.5% carbon, with possible additions of small percentages of other alloying elements, such as nickel and chromium, which are sometimes added to "Hadfield" steels.

Thus, the present improvements and discoveries provide for the ready and economical reclamation of damaged cold rolled high manganese steel strips of the lighter gauges to provide a finished material having the extremely high ductility characteristics of fully austenitic manganese steel, and having a bright color and sheen adapted for forming and bending operations because of the minutely pebbled texture thereof, the pebbled projections being smooth and rounded so as to appear bright to the naked eye.

Having now described the features of the invention, an embodiment of steps by which the invention may be carried out, the advantages and results attained by the invention, and the new discoveries made in connection with the treatment of high manganese steel; the new and useful methods, steps, treatments, arrangements and products, are set forth in the appended claims.

We claim:

1. The method of removing brittle decarburized surface metal layers from austenitized, high manganese, high carbon strip steel, including the steps of treating the strip in a dilute aqueous solution of up to 5% nitric acid by weight in water maintained at a temperature of from 180° to 210° F. for from 1 to 5 minutes, then treating the strip in a dilute aqueous solution of an alkali metal hydroxide of about 10% by weight in water maintained at a temperature of from 160° to 180° F. for from 15 to 45 seconds, and then treating the strip in a dilute aqueous solution of about 2% hydrochloric acid by weight in water maintained at a temperature of 140° to 180° F. for a few seconds.

2. The method of removing brittle decarburized surface metal layers from austenitized, high manganese, high carbon strip steel, including the steps of treating the strip in a dilute aqueous acid solution of up to 5% nitric acid by weight in water maintained at a temperature of 180° to 210° F. for from 1 to 5 minutes, then treating the strip in a dilute aqueous solution of about 10% sodium hydroxide by weight in water maintained at a temperature of from 160° to 180° F. for from 15 to 45 seconds, and then treating the strip in a dilute aqueous solution of about 2% hydrochloric acid by weight in water maintained at a temperature of from 140° to 180° F. for a few seconds.

3. The method of removing brittle, decarburized surface metal layers from austenitized, high manganese, high carbon strip steel, including the steps of treating the strip in a hot dilute aqueous solution of up to 5% nitric acid by weight in water containing from 1 to 5% ammonium nitrate by weight, then treating the strip in a dilute aqueous solution of an alkali metal hydroxide of about 10% by weight in water, and then treating the strip in a dilute aqueous solution of about 2% hydrochloric acid by weight in water.

4. The method of removing brittle decarburized

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surface metal layers from austenitized, high manganese, high carbon strip steel, including the steps of treating the strip in a hot dilute aqueous solution of up to 5% nitric acid by weight in water, then treating the strip in a dilute aqueous solution of an alkali metal hydroxide of about 10% by weight in water containing about $\frac{1}{2}$ % by weight of an alkali metal sulphide, and then treating the strip in a dilute aqueous solution of about 2% hydrochloric acid by weight in water.

5. The method of removing brittle decarburized surface metal layers from austenitized, high manganese, high carbon strip steel, including the steps of treating the strip in a hot dilute aqueous solution of up to 5% nitric acid by weight in water containing from 1 to 5% ammonium nitrate by weight, then treating the strip in a dilute aqueous solution of an alkali metal hydroxide of about 10% by weight in water containing about $\frac{1}{2}$ % by weight of alkali metal sulphide, and then treating the strip in a dilute aqueous solution of about 2% hydrochloric acid by weight in water.

6. The method of removing brittle, decarbu-

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rized surface metal layers from austenitized, high manganese, high carbon strip steel, including the steps of treating the strip in a hot dilute aqueous solution of up to 5% nitric acid by weight in water for from 1 to 5 minutes, then treating the strip in a hot dilute aqueous solution of an alkali metal hydroxide of about 10% by weight in water for from 15 to 45 seconds, and then treating the strip in a dilute aqueous solution of about 2% hydrochloric acid by weight in water for a few seconds.

7. The method of removing brittle, decarburized surface metal layers from austenitized, high manganese, high carbon strip steel, including the steps of treating the strip in a hot dilute aqueous solution of up to 5% nitric acid by weight in water for from 1 to 5 minutes, then treating the strip in a hot dilute aqueous solution of sodium hydroxide of about 10% by weight in water for from 15 to 45 seconds, and then treating the strip in a dilute aqueous solution of hydrochloric acid of about 2% by weight in water for a few seconds.

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