

UNITED STATES PATENT OFFICE

2,368,955

TREATMENT OF MANGANESE STEEL

Carl W. Weesner, Warren, Ohio, and Wallace
Bruce Leffingwell, Sharon, Pa., assignors to
Sharon Steel Corporation, Sharon, Pa., a corporation of Pennsylvania

No. Drawing. Application May 18, 1942,
Serial No. 443,452

8 Claims. (Cl. 148-18)

The invention relates to a 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.

Difficulties are encountered in the manufacture of cold rolled sheets and strips of the thinner gauges from high manganese or "Hadfield" steel, that is, steel containing from 10% to 20% manganese and from 1.00% to 1.50% carbon; and it is of great importance that these difficulties be avoided or eliminated, because large quantities of such high manganese strips and sheets are desired for the manufacture of helmets for the armed forces.

Helmet steel must be soft, ductile and have deep drawing qualities in order that helmets may be properly formed or drawn to the desired shape from high manganese sheets or strips. The sheets or strips may be as thin as .044 to .033 inch; and cold rolling operations must be performed to roll steel sheets and strips of such gauges. High manganese steel work hardens very quickly and can ordinarily only be cold rolled to a maximum of about 25% reduction. A heat treatment is then required after cold rolling to soften the same, and to enable further cold rolling.

The heat treatment of high manganese, high carbon steel to soften the same, or to restore ductility, or to permit further cold rolling after one cold rolling operation, consists in heating the steel to a temperature above the upper critical point, approximately 1800° F. to 1900° F. and preferably to about 1850° F. in order to dissolve brittle carbides and produce austenite; and in then quickly cooling the same, preferably by quenching in water.

This is because ductility in high manganese, high carbon steel depends upon the formation of gamma iron or austenite; and also upon the retention of gamma iron or austenite at room temperatures, obtained by a quick water quench. Also, the rapid cooling, as by the water quench, retains the carbon in solid solution in the austenite at room temperatures.

Although heat treatment is necessary to soften the steel and to restore ductility following a cold rolling operation, unfortunately steels of the "Hadfield" types are easily oxidized and decarburized at the surfaces when heated to the required temperature. Many bad surface conditions result from the oxidation or scaling; and the decarburization of the surface skin of the

metal sheets or strips, apparently causes surface embrittlement.

The decarburization or lowering of the carbon content of the surface skin of the metal is substantial and the carbon content at this region may become as low as .50% carbon, or less. When "Hadfield" steel is thus 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 epsilon iron and alpha iron, or both, in varying proportions. These decarburized surface layers containing epsilon iron and alpha iron are brittle and are formed with a myriad of small cracks; and the material though generally soft, has a ductility lower than desired.

When the metal is subjected to deep drawing operations, the small cracks develop and increase in size in the brittle surface layer, giving a characteristic granulated or "frosty" appearance. Thus the heat treatment which is intended to soften the steel and render it more ductile, on the contrary causes surface embrittlement and lowered ductility.

These undesirable surface characteristics are present in high manganese sheet steel made in accordance with sheet practice, but are more pronounced in strips and stripsheets made in accordance with strip practice. Sheets may be and usually are hot rolled to light gauges so as to require say only one cold rolling operation and one subsequent heat treatment operation. Strips and stripsheets after hot rolling ordinarily require a plurality of cold rolling operations, each followed by a heat treating operation, to reduce the strip or stripsheet thickness down to say .044 to .033 inch.

The formation of the brittle surface layers which are believed to be due to the presence, particularly, of epsilon iron therein, is cumulative with repeated heat treatments following cold rolling operations, so that the undesirable characteristics increase in magnitude, the thinner is the ultimate product, in making high manganese strip or stripsheet steel in accordance with strip practice.

These difficulties, as stated, result because of the excessive oxidation and decarburization of the surface of the material during the heat treating operations. The ultimate result is that the material has low ductility and an unsatisfactory surface and poor appearance because of the formation of the brittle layers on the surface, and because of the formation of scaling patterns. These results are contrary to the normal proper-

ties of austenitic manganese steel, which are those of austenite; namely low elastic limit, but great hardness and toughness and wearing power combined with much ductility.

Accordingly, the production of high manganese, high carbon steel in accordance with strip practice has been quite limited.

An object of the present invention is therefore 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, so that the normal properties of austenitic manganese steel may be obtained.

A further object of the present invention is to provide a commercially usable and satisfactory method of cold rolling high manganese steel in accordance with strip practice to gauges as thin as .044 to .033 inch in thickness.

It would be expected that the undesirable decarburized surface layers could be removed by continuing the pickling operation used for removing the scale after heat treatment, until a sufficient amount of the surface metal is eaten away or dissolved. However, the ordinary pickling acids, such as sulphuric or hydrochloric acids or combinations of the same, cannot be used on high manganese steel for metal removal without leaving an etched or pitted or sharp crag-like surface, in the same way that these acids and also nitric acid attack almost all other steels if used for metal removal.

However, we have discovered 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 the heat treating operation, and for removing the undesirable decarburized metal surface layers which are extremely detrimental to strength and ductility.

We have further discovered that certain other unexpected results occur when high manganese high carbon steel strips and sheets are so treated to remove scale and the brittle decarburized surface layers. Thus, we have found that seams, scratches, scale patterns, and rough or undesirable surface defects or imperfections which may be present on the surface of the metal due to previous rolling or due to the oxidation and scaling of the metal during heat treatment, are partially or totally removed, and the surface is greatly improved with a bright and lustrous appearance.

Thus, the resulting surface of the metal is bright in color, is free from sharp projections or indentations which might tend to injure ductility, and it has a greater usefulness, aesthetic appearance and corrosion resistance by virtue of the removal of undesirable surface conditions detrimental to strength and ductility.

Moreover, the resulting surface, when viewed with a magnifying glass is minutely "pebbled," which is a desirable characteristic, as a "pebbled" surface retains die lubricants which may be used during forming or drawing operations and provides an excellent surface for the retention or adherence of paint or other coatings which may be applied to the finished product.

It is therefore a further object of the present invention to provide a method of pickling high manganese steel with an acid for the removal of 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 a weak and relatively inexpensive acid for scale and brittle surface metal removal.

Likewise, it is an object of the present invention to provide a method of acid pickling high manganese steel, which not only removes scale and brittle surface metal, but which also partially or totally removes seams, scratches, scale patterns and surface defects or imperfections, leaving a bright or lustrous, smooth, minutely "pebbled" surface.

Furthermore, 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 new method of making cold rolled, light gauge, high manganese strip or stripsheet steel more quickly and more cheaply than it has been produced previously, by enabling the satisfactory commercial production thereof in accordance with strip practice.

And finally, it is an object of the present invention to provide a cold rolled, high manganese, strip and sheet steel product having a bright, lustrous, relatively smooth, pebbled surface, free of brittleness and having high ductility.

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, the step of subjecting the same to the action of a bath of a dilute aqueous solution of nitric acid, say up to 5% nitric acid by weight in water, at a temperature of about 140° to 200° F. for a sufficient time to remove scale on the surfaces thereof and to remove brittle surface metal layers thereon resulting from heat treatment, so as 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 described in detail as an embodiment of the way in which the method of the invention may be carried out, since the present invention enables the strip process to be used in the production of high manganese steel, and therefore enables great economies and speed in the manufacture of such steels to be obtained.

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 hot rolled strip is then pickled and cold rolled to maximum allowable reduction, which is approximately at 25% reduction for this type of steel, to say .079 inch in thickness.

The strip is then softened by heating it up to 1800° to 1900° F., preferably about 1850° F., and is then quenched in water. This treatment may be termed "austenitizing" and dissolves brittle carbides, retains carbon in solid solution, and renders the steel as fully austenitic as is possible. The steel may then be pickled in any usual way for scale removal, or may be subjected to the special pickling treatment of the present invention to be later described in detail.

The steel may then be cold rolled to maximum allowable reduction, which is approximately 25% reduction, down to say .058 inch in thickness, after which it is again heat treated and quenched, in the manner just described, followed by a usual pickling operation to remove scale, or by the special pickling operation of the present invention.

The steel may then be again cold rolled to maximum allowable reduction, say to .044 inch in thickness, which is one gauge of high manganese steel desired for helmet stock, after which it is heat treated, as stated, and if no more cold rolling is to be done, the cold rolled heat treated strip steel must then, in accordance with the present invention, be subjected to the special pickling operation of the present invention.

The special pickling operation may be used for any one of the pickling operations following any cold rolling step. The steel may be further cold rolled to lighter gauges such as .033 inch thick stock. In any event, the last pickling operation following the last cold rolling step must be the special pickling operation now to be described, in order to obtain the benefits of the discoveries and results of the present invention.

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

These undesirable surface layers are removed after heat treatment by the special pickling operation of the invention which may be carried out by passing the strip through and subjecting it to the action of a dilute solution of up to about 5% nitric acid by weight in water, maintained at a temperature of 140 to 200° F., preferably about 180° F. for say one to six minutes, depending upon the thickness of the surface metal to be removed and the temperature and concentration of the nitric acid bath.

That is to say, if the special treatment is only used once, the surface layers to be removed will be thicker, due to the cumulative effect of the plurality of austenitizing heat treatments to which the metal has been subjected, and the material will have to remain in the nitric acid bath longer for removing the undesirable surface layers.

If the acid concentration is too weak, the attack is too slow and a longer time of treatment in the bath will be required. If the acid concentration is too high, the attack is too vigorous and excessive fumes are formed. An increase in the temperature of the bath increases the rate of attack; and again, excessive fumes result when the temperature is too high.

The pickling and metal removal action of a fresh solution increases when the amount of dissolved iron is slightly increased; but thereafter, when the iron content of the bath is considerably increased, the action is sluggish and the bath

should be replenished with small additions of nitric acid.

When the concentration of dissolved metal in the bath becomes too high, somewhere between 3% to 5%, pitting may result, so that the bath must either be replaced or diluted with fresh water and nitric acid.

The thickness of metal to be removed depends upon the thickness of the brittle layers, which may be as thick as .001 inch, or may be considerably less than .0005 inch, on each side; and a slightly used bath of 5% nitric acid at 180° F. will dissolve from each side of the strip a thickness of approximately .0004 inch of metal per minute. The addition of ordinary inhibitors or catalysts may be made to the bath if desired.

The action of the bath can be speeded up, if desired, by using the bath as an electrolyte, and by using the metal as an anode and passing electric current through the solution to electrolytically treat the metal for removing scale and brittle surface metal layers. Likewise, the electrolytic treatment may be carried out by using the strip as a bi-polar electrode, in accordance with the method set forth in the L. H. Wilson Patent No. 2,197,653.

If the bath is operated as an electrolyte, the temperature may be maintained at about 60° F. to 150° F., preferably about 120° F. for the required length of time. With a comparatively small current density, a slightly used bath will dissolve the metal electrolytically at 120° F. at the rate of approximately .0004 inch per minute. Current density is not important because it only speeds up the rate of metal removal, since the bath will operate satisfactorily without being operated as an electrolyte.

After the metal has been subjected to the acid attack, a thin brown sludge or precipitate may remain on the surface, but this sludge may be easily removed by scrubbing the surfaces with any usual scrubbing equipment.

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. After the scrubbing operation, the strip is finally washed in water and dried by hot air blasts or other means, and oiled if desired.

When high manganese, high carbon steel trips are made as outlined above, without using the special pickling operation of the present invention, the finished material is generally soft, well annealed, and free from carbides; but the surfaces are poor, the ductility is lower than desired, and a granulated or "frosty" condition occurs when the material is drawn.

Hardness tests made with various penetrations or depths to show the relative hardness at various depths, indicated that the brittle surface layer is not necessarily due to a hard constituent such as martensite.

Samples were reannealed to determine whether or not the ductility could be improved by changes in the heat treating practice; but these tests indicated that changes in the heat treatment did not improve ductility or eliminate the brittle or "frosty" surface conditions.

These and other tests did show, however, that excessive oxidation of the surface and surface embrittlement go hand in hand; and analysis of the metal at various depths indicated that the carbon content of the surface metal was mate-

rially lower than that of the core of the metal. Samples having decarburized surfaces were again carburized to materially increase the carbon content of the surface layers and were then heat treated so that the carbon content of the surface layers was approximately that of the core, somewhere between 1% and 1.5% carbon. The result was exceptionally good ductility and a disappearance of the "frosty" surface conditions, indicating that the brittle surface is produced by depletion of the surface metal carbon. However, it is not feasible in the production of high manganese, high carbon steel strips to eliminate surface embrittlement by a carburizing step following the final cold rolling and heat treatment.

Decarburization alone does not explain the existence of surface embrittlement found in heat treated "Hadfield" steel. The phenomenon is apparently due to some radical structural change, which occurs coincident with the lowering or depletion of the carbon content. As previously stated, when the carbon is materially lowered, austenite is not completely retained upon cooling, but some of it decomposes into alpha iron or epsilon iron, or both, at approximately 400° F. These alpha and epsilon phases, especially the latter, must be expected to be brittle, and the brittle surface layer probably consists of three phases—alpha, gamma and epsilon irons; which is apparently the structural change occurring with a depletion of the carbon in the surface layers.

The metallographic identification of alpha and epsilon iron is difficult, but is indicated by the so-called "Widmanstätten" pattern. In samples where the brittle surface layer is present, we have found that the surface metal and core metal responds differently to different etchants, and careful etching technique reveals that the decarburized surface layer contains considerable "Widmanstätten" structure.

As to the heat treating cycle, the best results will be obtained and the surface embrittlement maintained at a minimum by avoiding oxidizing atmospheres, by annealing at the lowest temperature and fastest speed required to dissolve the carbides, and by quenching immediately in water. Oxidizing atmospheres and violently agitated atmospheres tend to increase scaling and surface embrittlement, and the best atmosphere is a quiet atmosphere of reducing gas.

"Hadfield" steels must be heated to above the upper critical point, 1800° F. to 1900° F. in order to dissolve carbides and produce austenite, but higher temperatures than absolutely necessary increase scaling and surface embrittlement. In general two minutes heat treatment at about 1850° F., or between 1850° F. and 1900° F., one minute, coming to temperature and a one minute soak, is sufficient. Increasing the time in the furnace produces heavier scale and increases surface embrittlement and "frost."

Quenching in water is better than air cooling or quenching in cold brine, because excessively drastic cooling increases hardness, air cooling increases scale and surface embrittlement, and slow cooling precipitates carbides and makes a brittle product.

The result of the special pickling treatment of the present invention following heat treatment, is to increase the toughness, strength and ductility of the metal because of the removal of scale, seams, scratches and other surface imperfections detrimental to strength and ductility; because of

the removal of the brittle surface layers due to the precipitation of alpha or epsilon iron or both, in the decarburized surface metal, the brittle layers being extremely detrimental to strength and ductility; and because of the formation of a smooth lustrous surface of minutely "pebbled" contour.

The final product is fully austenitic in character with the related characteristics of austenitic manganese steel fully developed entirely throughout the metal of the strip and the improved surface is a superior base for die lubricants in forming operations, and for paints or other coatings applied to the finished product. This surface is much more smooth and ductile than the usual pickled surfaces which contain many sharp projections and irregularities detrimental to strength and ductility. Actual tests have shown that the treatment increases the ductility of the material as much as 10% or more.

We therefore term the special pickling treatment of the present invention a "pickle polishing" operation, because it not only removes scale, but also removes metal and results in a smooth metal surface finish, which is not etched or pitted; and this pickle polishing operation is carried out with a weak and inexpensive acid, which easily and economically smoothes out surface imperfections and removes the brittle surface layers produced by heat treating "Hadfield" type steels and produces a light gauge cold rolled "Hadfield" steel of high ductility and bright appearance.

While the process and product have been described in connection with the manufacture of strip steel or strip sheets in accordance with strip practice, the present invention is also applicable to the manufacture of other high manganese steel products such as sheet steel in accordance with sheet practice, wherein the "pickle polishing" operation would be carried out following the final cold rolling and heat treatment operations, of which there may be only one or two in sheet practice, to remove the 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 "strips" 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, strip sheets, sheets, plates, bars, rounds, wire, forgings or castings and the like, in order to remove scale, seams, scratches, brittle surface layers and other surface imperfections, to provide a surface much improved over that produced by usual pickling methods.

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 contains 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 dis-

coveries provide for the ready and economical manufacture of high manganese steel strips of the lighter gauges having extremely high ductility characteristic 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, and an embodiment of steps by which the invention may be carried out, and 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.

I claim:

1. In the manufacture of thin gauge, cold rolled, heat treated, high manganese, high carbon, strip steel and the like; the step of subjecting such steel strip after cold rolling and austenitizing heat treatment to the action of a dilute aqueous solution of up to approximately 5% by weight nitric acid to remove scale and surface layers of brittle metal formed by heat treatment, and to render the steel fully austenitic throughout.

2. In the manufacture of heat treated, high manganese, high carbon, strip steel and the like; the steps of heat treating high manganese, high carbon, strip steel by heating the same to between 1800° F. and 1900° F., and then quenching in water; and then pickle polishing the steel in a dilute aqueous solution of up to approximately 5% by weight nitric acid to remove scale and surface metal and to form smooth bright surfaces thereon.

3. The method of treating thin gauge, cold rolled, austenitized, high manganese, high carbon, strip steel and the like, to remove scale, brittle surface layers, scratches, scale patterns and surface defects, and to increase the ductility thereof; which includes pickling such steel in a dilute aqueous solution of up to approximately 5% by weight nitric acid to remove scale, and continuing the pickling operation to uniformly dissolve the thin layers of brittle surface metal thereon, and to form smooth, bright, lustrous, minutely "pebbled" surfaces thereon.

4. In the manufacture of thin gauge, cold rolled, heat treated, high manganese, high carbon, strip steel and the like; the steps of heat

treating cold rolled, high manganese, high carbon, strip steel by heating the same for up to about 2 minutes to between 1800° F. and 1900° F., and then quenching in water; and then removing surface metal layers of the strip by pickling in a dilute aqueous solution of up to approximately 5% by weight nitric acid to eliminate decarburized surface metal containing alpha and epsilon iron formed by the heat treatment.

5. In the manufacture of heat treated, high manganese, high carbon, strip steel and the like; the steps of heat treating high manganese, high carbon, strip steel by heating the same to between 1800° F. and 1900° F., and then quenching in water; and then pickle polishing the steel in a solution of 1% to 5% by weight of nitric acid in water at a temperature of from 140° F. to 200° F. for 1 to 6 minutes to remove scale and surface metal.

6. In the manufacture of heat treated, high manganese, high carbon, strip steel and the like; the steps of heat treating high manganese, high carbon, strip steel by heating the same to between 1800° F. and 1900° F., and then quenching in water; and then pickle polishing the steel in a solution of approximately 5% nitric acid by weight in water at a temperature of about 180° F. for from 1 to 6 minutes to remove scale and surface metal and to form smooth bright surfaces thereon.

7. In the manufacture of heat treated, high manganese, high carbon, strip steel and the like; the steps of heat treating high manganese, high carbon, strip steel by heating the same for upwards of 2 minutes at a temperature of from 1850° F. to 1900° F., and then quenching in water; and then pickle polishing the steel in a dilute aqueous solution of up to 5% nitric acid by weight in water to remove scale and surface metal and to form smooth, bright surfaces thereon.

8. In the manufacture of heat treated, high manganese, high carbon, strip steel and the like; the steps of heat treating high manganese, high carbon, strip steel by heating the same for about 2 minutes at a temperature of about 1850° F., and then quenching in water; and then pickle polishing the steel in a solution of 1% to 5% nitric acid by weight in water at a temperature of about 180° F. for from 1 to 6 minutes to remove scale and surface metal and to form smooth bright surfaces thereon.

CARL W. WEESNER.

W. BRUCE LEFFINGWELL.