United States Patent

[11] 3,615,903

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[21] Appl. No. 764,923
[22] Filed Oct. 3, 1968
[45] Patented Oct. 26, 1971

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[54] **HIGH-PURITY FERROUS MATERIAL AND METHOD OF MAKING IT**
11 Claims, No Drawings

[52] U.S. Cl. 148/12.1, 148/16, 148/122
[51] Int. Cl. C21d 1/74
[50] Field of Search 148/12.1, 16, 122

[56] References Cited

UNITED STATES PATENTS

3,379,581	4/1968	Kohler et al.	148/122

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ABSTRACT: A high-purity ferrous material and method of making it, whereby the ferrous material is hot rolled to sheet or coil thicknesses. Thereafter, the ferrous material is descaled and may be further reduced in thickness by cold rolling when necessary. The hot rolled or hot and cold rolled ferrous material is then coated with any of the annealing separators described below and annealed at a temperature of from about 1,900° F. to about 2,500° F. in an atmosphere of 100 percent hydrogen or a hydrogen bearing atmosphere capable of removing impurities to the desired low levels. When the proper relationships are maintained with respect to initial manganese and sulfur contents, gauge, nature of the annealing separator, dew point of the annealing atmosphere, composition of the annealing atmosphere, annealing temperature and soak time, a product is produced having a composition comparing favorably to or surpassing that of typical electrolytic iron.

HIGH-PURITY FERROUS MATERIAL AND METHOD OF MAKING IT

BACKGROUND OF THE INVENTION

1. Field of Invention

The invention relates to a high-purity ferrous material and more particularly to a high-purity ferrous material, the composition of which compares favorably with or excels that of typical electrolytic iron. The term "ferrous material" as used hereinafter and in the claims is intended to include ingot iron and plain carbon steel.

2. Description of the Prior Art

The product of the invention has many applications and may be used wherever a ferrous material low in sulfur and nitrogen would be desirable. For example, the product may be used in special types of welding operations, in the manufacture of shaped charge cones and as a charge material in various melting procedures. While not intended as a limitation on the invention, for purposes of an exemplary showing the high-purity ferrous material of the present invention will be described with respect to its use as a charge material in compounding air-melted and vacuum-melted ferrous alloys.

Heretofore, when melting steels by processes including vacuum induction melting techniques, alloy steel producers have used electrolytic iron as a charge material in compounding the heat analyses when high-purity alloys were desired. Vacuum induction melting techniques have come into widespread acceptance in the industry, because materials produced thereby have a much lower gas and inclusion content and are particularly desirable for high stress level applications such as generator and turbine rotors, aircraft uses and the like.

A primary problem in the production of alloys by these techniques lies in the fact that electrolytic iron is a very expensive charge material, and hence the cost of alloys made therefrom is relatively high.

In ordinary steel-making processes it is the usual practice to use a flux or slag in an open hearth furnace or an electric furnace. The slag, composed of lime and various other substances, will remove sulfur from liquid iron as a result of an interface reaction between the slag which floats on top of the bath and the liquid iron which is in contact therewith. However, in vacuum melting the use of a slag is undesirable for a number of reasons. For example, the amount of space inside the vacuum container is limited and the nature of the slagging reaction is such as to cause the slag to clog the vacuum melting facility. Thus, as indicated above, prior art melters have gone to electrolytic iron as the source of the iron component in vacuum-melted ferrous alloys such as precipitation hardening steels and the like.

It has, however, been discovered that a superior charge material for use in the manufacture of air-melted and vacuum-melted ferrous alloys can be prepared from ingot iron or plain carbon steel. As used herein, the terms "ingot iron" and "plain carbon steel" refer to ferrous materials differing from each other primarily in that ingot iron has an initial manganese content of about 0.06 percent or less and plain carbon steel has an initial manganese content greater than about 0.06 percent. Both ingot iron and plain carbon steel contain the usual impurities in residual amounts, coincident with their manufacture, the balance being iron.

While the products of the present invention may be produced using plain carbon steel as a starting material, ingot iron is the preferred starting material since it is the purest iron available from the inexpensive, large-volume steel-making processes. In instances when a higher manganese content is desired in the charge material, plain carbon steel can be used.

In accordance with the teachings of the present invention, an excellent charge material is formed by removing impurities from ingot iron or plain carbon steel in sheet or coil form. The primary impurity under consideration is sulfur. In addition, however, the nitrogen, phosphorus, oxygen and carbon contents of the starting material may be lowered as well.

It has hitherto been known, as taught in U.S. Pat. No. 1,586,543, that certain of these impurities may be removed from some metals by coating the metals with carbon, silicon, alkaline earth metal oxides or, silicides of various metals and annealing the metals at a high temperature in hydrogen or a hydrogen-bearing gas.

More recently, prior art workers involved in the production of certain types of oriented silicon-irons have learned that coating silicon-irons with magnesia or calcium oxide and subjecting them to a high-temperature anneal will result in the removal of sulfur therefrom.

In U.S. Pat. No. 3,379,581 it is taught that the sulfur content of the silicon-iron stock may be reduced to an extremely low value if the stock is coated with an annealing separator consisting essentially of magnesium oxide and from about 2 percent to about 10 percent of calcium oxide and is subjected to a high-temperature anneal.

Finally, the use of calcium oxide, magnesia, alumina and various admixtures of these materials has for many years been proposed to serve as annealing separators when box annealing steel sheet for one reason or another. However, the use of such separators was directed primarily to preventing the sheets from sticking together during high-temperature anneals.

The subject matter of the present invention relates to the discovery that if ingot iron or plain carbon steel is rolled to proper thickness, coated with an appropriate annealing separator and annealed under desired conditions, a charge material may be produced having a composition comparable to or superior to that of typical electrolytic iron. This is particularly true when the proper relationships are maintained with respect to initial manganese and sulfur contents of the starting ferrous material, the gauge to which the starting material is rolled, the annealing separator used, the dew point in the annealing furnace, the composition of the annealing atmosphere, the temperature of the anneal and the soak time. In the manufacture of electrolytic iron the oxygen and nitrogen content of the base metal is unaffected. The ferrous material of the present invention had a reduced oxygen content and may have a reduced nitrogen content. Nitrogen content has a great effect on certain properties of steels. The high nitrogen content of electrolytic iron cannot easily be removed by air-melt and vacuum-melt processes.

The high-purity ingot iron or plain carbon steel of the present invention comprises an excellent charge material in the manufacture of air-melted and vacuum-melted ferrous alloys and can be produced at a cost far less than that entailed in the production of electrolytic iron. Where used as a charge material in an air-melt process, the ferrous material taught herein reduces furnace time because double slagging is not required to lower the sulfur content of the final product.

SUMMARY OF THE INVENTION

The high-purity ferrous material of the present invention is produced by first hot rolling ordinary ingot iron or plain carbon steel to sheet or coil thicknesses. The ferrous material is descaled and may be further reduced in thickness by cold rolling, when necessary. The ferrous material at final gauge is coated with an annealing separator such as calcium oxide, magnesium oxide, lime, dolomite, combinations of these materials or materials, inert in this process, such as alumina. Even a mechanical separator may be used. The annealing separator is applied in any suitable manner. The annealing separator coating should provide continuous separation of the ferrous material sheets or coil convolutions and preferably should contain some coarse material to aid in permitting adequate passage of an annealing atmosphere between the sheets or coil convolutions. The coated material is then annealed, resulting in the reduction of the level of sulfur, together with the levels of phosphorus, oxygen and carbon. The nitrogen level may also be reduced depending upon the composition of the annealing atmosphere. The anneal is car-

ried out as a temperature of from about 1,900° F. to about 2,500° F. The annealing atmosphere and the dew point are closely regulated, and the ferrous material is soaked at temperature.

Upon cooling, the high-purity ferrous material is cleaned by appropriate means to remove any remaining annealing separator.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to compare favorably with or to be superior to typical electrolytic remelt stock, the ferrous material must be treated in such a way as to reduce the levels of the above listed impurities to the following maximum values:

Sulfur	0.004%
Nitrogen	0.004%
Phosphorus	0.005%
Oxygen	0.070%
Carbon	0.018%

It has been discovered that the production of the high-purity ferrous material of the present invention depends upon a number of interrelated factors. These factors include the initial manganese and sulfur contents of the starting material, the gauge to which the starting material is rolled, the nature of the annealing separator applied to the starting material at final gauge, the dew point maintained within the furnace during the annealing step, the composition of the annealing atmosphere, the temperature of the anneal and the soak time. Each of these factors will be discussed, in turn.

The initial manganese content of the ferrous material has been discovered to bear an important relationship to the ease with which the desired final level of sulfur can be reached during an anneal. This is true because the higher the initial manganese content, the greater the tendency for the formation of manganese sulfides. Manganese sulfides comprise relatively stable inclusions difficult to break down even at the annealing temperatures contemplated.

For this reason, the initial manganese content should preferably be as low as possible. For the same reason, ingot iron is preferred over plain carbon steel in the manufacture of the high-purity ferrous material of the present invention. Thus, while the initial manganese content should preferably be not more than about 0.06 percent, the high-purity ferrous material of the present invention has been successfully and consistently made in instances where the starting material was plain carbon steel having an initial manganese content of about 0.5 percent.

While all of the above-listed factors are interrelated, the final gauge and the soak time are of particular importance with respect to the initial manganese content. Thus, the higher the initial manganese content, the thinner the final gauge of the starting material should be and/or the longer should be the soak time, as will be discussed hereinafter.

It will be understood by one skilled in the art that the initial sulfur content of the ingot iron should be as low as possible, since a low initial sulfur content means less sulfur required to be removed. When the initial sulfur content in the starting material is unusually high, two annealing steps may be required to reach the desired final sulfur level.

The ingot iron is first hot rolled to sheet coil thicknesses. The base metal can be treated in thicknesses up to about 0.2 inch, , although the thinner the gauge, the more rapid the desulfurization, requiring less time at temperature during the annealing step. For this reason, the base metal may be further cold reduced if desired. Cold reduction to a thickness of about 0.025 inches will be required when the manganese content is very high, i.e., up to about 0.5 percent. In general, however, cold rolled gauges have not been found necessary when the initial manganese content is at the preferred level of about 0.06 percent or less, and excellent results have been achieved when the base material was hot rolled to a thickness of from about 0.050 inches to about 0.080 inches. Soak time will also have an important bearing on the gauge to which the ferrous starting material must be rolled. For example, excellent results have been achieved at a gauge of 0.050 inch with a starting material having a manganese content of 0.13 percent, when a relatively long soak time of 96 hours was used.

The ferrous starting material, having been hot rolled to final thickness, or prior to a cold rolling step, is descaled. When final thickness is reached by hot rolling, or after a cold rolling step, the starting material is mechanically cleaned and may be coiled or cut into sheets or suitable size for box annealing. The coiled or sheet material is then coated with an annealing separator. A number of annealing separators have been found to be particularly suited to the purposes of the present invention. For example, calcium oxide, magnesia, lime or dolomite and the combinations of these materials have been used with success. As a nonlimiting example, excellent results were achieved with burnt dolomite, comprising (by weight) 40–50% CaO, 30–40% MgO, 0–10% SiO_2, 0–12% Al_2O_3 and 0–0.3% S. The process can also be carried out using alumina or a similar separating material inert in this process. It is also within the scope of the invention to use mechanical separators.

The coating may be applied in any known manner. For purposes of an exemplary showing, excellent results have been achieved when the coating was applied as an aqueous slurry by any suitable means such as dipping, roller coating or the like. It is important that the coating create continuous separation of the sheets or coil convolutions because the temperature of the anneal will be sufficiently high to cause welding of the sheets or convolutions together, in the absence of a continuous coating.

While the thickness of the annealing separator is not critical, it should be applied in as thick a coating as possible. The thickness should preferably be on the order of 0.002 inches. In addition, it has been found that the incorporation of coarsely ground material such as limestone or alumina is helpful in permitting the annealing atmosphere to penetrate between the sheets or convolutions. Such coarse material will provide adequate mechanical spacing of the sheets or convolutions and will prevent compacting of the separator material. If the particle size of the coarsely ground material is too great, the particles will tend to imbed themselves in the surfaces of the sheets or coil convolutions. For this reason, the particles should preferably have a diameter of not more than about twice the coating thickness. It is a primary function of the annealing separator to permit the annealing atmosphere to contact the surfaces of the sheets or coil convolutions and to circulate between them. The coarse material may be applied in any suitable manner. For example, it may be added to the annealing separator slurry, or it may be sprinkled on the surfaces of the sheets or coil convolutions together with the separator material in dry powder form.

Finally, the annealing separator may contain a nitrogen getter if desired, to reduce the nitrogen level in the ferrous material.

The coated ferrous material is then box annealed. The annealing step should begin immediately following the coating operation to prevent further hydration of the annealing separator material and possible pickup of carbon dioxide by the separator. These problems may be obviated, in part at least, by using one or more of the above-described annealing separator materials in their nonhydrating form.

The heat-up period should be conducted slowly. Care must be taken to control the dew point to prevent break down of the annealing separator material and consequent fusion of the sheets or convolutions. Particular attention should be given to the dew point as the furnace temperature climbs above 700° F. and again as the furnace temperature climbs above 1,100° F., the temperatures at which magnesium hydroxide and calcium hydroxide begin to dehydrate. The use of separator materials which will tend to give off mechanically or chemically held water during the heat-up period requires careful dew point control to prevent formation of iron oxide at the surfaces of

the sheets or coil convolutions. Any iron oxide thus formed can combine with a calcium oxide or magnesia annealing separator to produce a molten slag which will inhibit removal of impurities from the ferrous material and will tend to run from between the sheets or convolutions permitting the welding thereof.

During the heat-up period of the anneal, the heating rate should be adjusted so as to allow for the removal of any water vapor evolved from the annealing separator, the heating rate will depend upon the type of furnace used and the capacity of the drying equipment employed. Such heating rate adjustment is well within the skill of the worker in the art.

After purging the annealing furnace with a nonexplosive atmosphere, a 100 percent hydrogen atmosphere, or a hydrogen-bearing atmosphere, should be introduced into the furnace at the lowest possible temperature believed to be safe. While not intended to constitute a limitation on the present invention, excellent results have been achieved using a purging atmosphere comprising hydrogen and nitrogen, with a preponderance of nitrogen (as for example 5 percent hydrogen and 95 percent nitrogen).

While a 100 percent hydrogen atmosphere is preferred for the anneal, a hydrogen-bearing atmosphere, which will be desulfurizing and which will prevent nitrogen pickup by the ferrous material, may be used with excellent results. Such a hydrogen-bearing atmosphere may be so compounded as to be denitriding, when desired.

At all times a maximum recirculation flow of the annealing atmosphere should be maintained and conditions oxidizing to the ferrous material should be avoided. Maximum recirculation flow of the annealing atmosphere is aided by the annealing separator, as mentioned above, and oxidizing conditions are avoided by use of a reducing atmosphere and by control of the dew point. While not intended to be a limitation on the invention (since it will vary with the operating conditions, type of separator material and the like) maintenance of a dew point of about 30° F. or less has been found satisfactory for most conditions.

When the final temperature of from about 1,900° F. to about 2,500° F. (preferably from about 2,100° F. to about 2,200° F.) is reached, the ferrous material is caused to soak at temperature. The annealing temperature is one of the factors mentioned above which is important in determining the final sulfur level which may be achieved during the anneal. In general, the higher the annealing temperature (within the above stated ranges) the more rapidly desulfurization will take place, all other factors remaining the same. Given the above range, one skilled in the art can readily determine an appropriate annealing temperature, depending upon the other factors mentioned above and the capacity of the furnace being used. When an annealing temperature is chosen below about 2,000° F., consideration should be given to the initial copper content of the ferrous material. At these temperatures copper may form copper sulfides which, like manganese sulfides, comprise relatively stable inclusions difficult to break down.

The soak time is another of the above-mentioned interrelated factors which must be considered. The length of time of the soak at temperature will depend upon the final gauge of the sheets or coil convolutions being annealed, the nature of the annealing separator being used, the initial composition of the ferrous material, the annealing temperature and the final sulfur level sought. Depending upon these factors, the soak time can vary between about 24 hours and about 140 hours.

After the soak at temperature, the ferrous material should be allowed to cool below about 800° F. while still maintaining the 100 percent hydrogen atmosphere or the hydrogen-bearing atmosphere. Thereafter, the furnace may be purged with nitrogen or other nonexplosive atmosphere. It is important to maintain the hydrogen-bearing atmosphere or the 100 percent hydrogen atmosphere until the ferrous material reaches a temperature such that nitrogen will no longer be picked up by it. The annealed, high-purity ferrous material should then be cleaned. Any suitable mechanical or chemical cleaning method may be used. A thorough wet scrubbing operation with steel or bristle brushes is satisfactory, although a pickling operation with hydrochloric or sulfuric acid has been found more reliable. In extreme cases, both methods may be used. It is important that all of the annealing separator be removed from the ferrous material. If any of the separator remains on the ferrous material and is included in the ultimate melt charge, some of the impurities which have been removed from the ferrous material will then be present in the charge through the remaining annealing separator.

Depending upon its ultimate use, the ferrous material of the present invention may be commercially produced in sheet or coil form. In addition, the product of the present invention may be sheared into convenient sizes for use as charge material or the like.

The exact mechanism by which the various named impurities are removed is not thoroughly understood. While not wishing to be bound by theory, evidence indicates that the nitrogen is removed solely by the hydrogen annealing atmosphere in the form of ammonia gas. This is believed to be true because all of the above mentioned slurries remove nitrogen satisfactorily and to substantially the same degree.

The sulfur removal, however, can apparently be aided by the annealing separator itself. Depending, of course, on the nature of the annealing separator used, it is believed that sulfur is removed, in part at least, by the formation of calcium sulfide and/or other magnesium sulfide. The hydrogen annealing atmosphere removes some of the sulfur by the formation of hydrogen sulfide gas. While all of the above-mentioned annealing separators are adequate for the purposes of the present invention, it has been found that sulfur will be removed to a given level faster when dolomite and calcium oxide separators are used than when magnesia, aluminum oxide or mechanical separators are employed.

EXAMPLE I

Five 10,000 lb. ingots of ingot iron were hot rolled to 0.080 inch thickness. The hot rolled ingot iron was sheared into sheets, pickled in hot sulfuric acid to remove oxide scale and coated with a slurry of burnt dolomite (MgO—CaO). The coated sheets were passed through a drying furnace to drive off the excess water on the sheets and in the coating. Some hydration of the magnesium oxide and calcium oxide occurred, causing a portion of the coating to be made up of magnesium hydroxide and calcium hydroxide.

The coated sheets were placed in an annealing furnace. Oxygen was purged from the furnace by a 7 percent hydrogen—93 percent nitrogen atmosphere. Heating was started at 20° F. per hour. The atmosphere was recirculated through silica gel drying beds to remove water being driven off from the annealing separator.

At 750° F., the entering atmosphere was adjusted to 100 percent hydrogen. Heating was continued unless the dew point increased to above 25° F. When this occurred, further heating was stopped until the dew point dropped. When the temperature reached 2,200° F., the sheets were soaked for 100 hours. There after, heating was discontinued and the sheets were cooled. When the sheets reached a temperature of 750° F. the 100 percent hydrogen atmosphere was replaced by a 100 percent nitrogen atmosphere.

When the sheets had cooled, they were placed in a bath of dilute hydrochloric acid and allowed to soak in order to soften the annealing separator coating. Thereafter, the sheets were pickled in sulfuric acid, scrubbed clean and dried.

The cleaned sheets were sheared to a convenient size and bundled in 5,000 lb. bundles for charging into a melting furnace.

The initial and final chemistry of the ingot iron is given in per cent in the following table:

TABLE I

Chemistry	C	S	P	N	O	Mn	Cu
Initial	.026	.019	.005	.004	.070	.026	.036
Final	.002	.002	.004	.001	.004	.026	.036

It will be noted from the above table that the carbon, sulfur, nitrogen and oxygen contents of the ingot iron were considerably reduced. One skilled in the art will recognize that the final chemistry of the ingot iron of the present invention was superior to that of the typical electrolytic iron.

EXAMPLE II

Plain carbon steel having an initial manganese content of 0.40 percent was hot rolled to 0.088 inches. The hot rolled material was sheared into sheets, pickled in hot sulfuric acid to remove oxide scale and coated with alumina particles.

The coated sheets were stacked in a laboratory annealing furnace. The furnace was purged with a 100 percent nitrogen atmosphere and then a 100 percent hydrogen atmosphere was introduced and continuously renewed. The furnace was heated at a rate of 50 F. per hour to 2,200° F. and the sheets were soaked for 96 hours. Thereafter, the sheets were cooled to room temperature in the 100 percent hydrogen atmosphere. The furnace then purged with a 100 percent nitrogen atmosphere and the sheets were renewed. The annealing separator was mechanically removed from the sheets.

The initial and final chemistry of the plain carbon steel is given in per cent in table II below:

TABLE II

Chemistry	C	S	P	N	O	Mn	Cu
Initial	.060	.012	.004	.004	.050	.40	.68
Final	.001	.004	.003	.0005	.001	.40	.68

It will be seen from table II that the final chemistry of the plain carbon steel was superior to that of the typical electrolytic iron, despite the fact that the initial manganese content of the plain carbon steel was relatively high.

EXAMPLE III

This example involves a total of 96 samples divided into four groups. The first group comprised 24 samples of ingot iron having an initial manganese content of 0.04 percent. The other three groups each comprised 24 samples of plain carbon steel having an initial manganese content of 0.13 percent, 0.22 percent and 0.44 percent respectively.

Six samples from each group were hot rolled to 0.100 inches; six samples from each group were hot rolled to 0.075 inches; six samples from each group were hot rolled to 0.050 inches and six samples from each group were first hot rolled to 0.050 inches and then cold rolled to 0.025 inches. All samples were pickled in hot sulfuric acid after the hot rolling step. All of the samples were then coated with burnt dolomite, dried and annealed a laboratory furnace in 100 percent hydrogen at 2,200° F.

Prior to the anneal, the furnace had been purged with an atmosphere comprising 7 percent hydrogen and 93 percent nitrogen. The 100 percent hydrogen atmosphere was introduced into the furnace at room temperature and the furnace temperature was raised 400° F. per hour until the final temperature was reached. No significant rise in dew point occurred when the magnesium and calcium oxides dehydrated because the 100 percent hydrogen atmosphere was continuously renewed rather than recirculated.

Two samples of each gage and manganese content were soaked at temperature for 24 hours. Similarly, two identical samples of each gage and manganese content were soaked at temperature for 48 hours and two such samples were soaked at temperature for 96 hours.

In all instances the samples were cooled in the 100 percent hydrogen atmosphere to room temperature. The furnace was then purged with an atmosphere of 7 percent hydrogen and 93 percent nitrogen. All samples were mechanically cleaned and pickled in dilute hydrochloric acid to remove the annealing separator.

The results are summarized in table III below wherein the first column indicates the soak time, the second column sets forth the gauge and the remaining four columns show the final sulfur contents for the samples having an initial manganese content of 0.04 percent, 0.13 percent, 0.22 percent and 0.44 percent, respectively. Each of the final sulfur values in table III represents an average for a pair of samples.

TABLE III

Soak time in hours	Gauge in inches	Final sulfur contents in percent for samples having an initial manganese content of: .04	.13	.22	.44
24	.100	.0165	.028	.0315	.0315
24	.075	.0125	.021	.0295	.0290
24	.050	.0029	.016	.0210	.0280
24	.025	.0005	.0005	.0040	.0155
48	.100	.011	.0235	.0270	.0315
48	.075	.004	.0165	.0265	.0290
48	.050	.001	.006	.0155	.0225
48	.025	.0005	.001	.001	.002
96	.100	.0055	.0175	.0245	.0265
96	.075	.001	.0125	.0190	.0235
96	.050	.0007	.0009	.0080	.0165
96	.025	.0005	.0005	.0005	.0005

Table III clearly illustrates the interrelationships of soak time, gauge and initial manganese content with respect to the final sulfur content of the ferrous material.

In those samples where the initial manganese content was 0.04 percent good results were achieved with a 24-hour soak when the gauge 0.050 inches or less. When the soak time was increased to 48 and 96 hours, excellent results were obtained at a gauge of 0.075 inches or less. Extremely low sulfur values were achieved in 48 hours at a gauge of 0.025 inches and in 96 hours at gauges of 0.050 inches and 0.025 inches.

When the initial manganese contents were 0.13 percent and 0.22 percent, good results were achieved in soak times of 24 hours and 48 hours at the 0.025 inch gauge. At a soak time of 96 hours, extremely low sulfur values were achieved in the 0.13 percent manganese material at gauges of 0.050 inches and 0.025 inches and in the 0.22 percent manganese material at 0.025 inches.

The last column of table III represents final sulfur values for the ferrous material having an initial manganese content of 0.44 percent. Even at this high manganese content, excellent results were achieved when the material was first hot rolled to 0.050 inches, then cold rolled to 0.025 inches and soaked for 48 or 96 hours.

Modifications may be made in the invention without departing from the spirit of it.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of producing high-purity ferrous stock from a starting material chosen from the class consisting of ingot iron and plain carbon steel having an initial manganese content up to about 0.5 percent, comprising the steps of reducing the thickness of said stock to a final gauge of at least 0.2 inches, descaling said stock, applying an annealing separator to said stock, annealing said stock in an atmosphere of 100 percent hydrogen, or a hydrogen-bearing atmosphere having a nitrogen content such as to prevent nitrogen pickup by said stock, conducting said anneal at a temperature of from about 1,900° F. to about 2,500° F., maintaining the dew point of said annealing atmosphere at a level such as to prevent the formation of iron oxide at the surfaces of said stock, and maintaining said stock at temperature for from about 24 hours to about 140 hours, whereby to produce a ferrous stock having a final sulfur content of about 0.004 percent or less.

2. The process claimed in claim 1 wherein said initial manganese content is below about 0.06 percent.

3. The process claimed in claim 1 wherein said stock is reduced to a final gauge of from about 0.025 inches to about 0.080 inches.

4. The process claimed in claim 1 wherein said anneal is conducted at a temperature of from about 2,100° F. to about 2,200° F.

5. The process claimed in claim 1 wherein said annealing separator is chosen from the class consisting of calcium oxide, magnesia, lime, dolomite and combinations thereof.

6. The process claimed in claim 1 wherein said annealing separator is alumina.

7. The process claimed in claim 1 wherein said annealing separator is a mechanical separator.

8. The process claimed in claim 1 wherein said dew point of said annealing atmosphere is maintained at a level of 30° F. or less.

9. A method of producing high-purity ferrous stock from a starting material chosen from the class consisting of ingot iron and plain carbon steel having an initial manganese content up to about 0.5 percent, comprising the steps of reducing the thickness of said stock to a final gauge of at least 0.2 inches, descaling said stock, applying an annealing separator to said stock, annealing said stock in an atmosphere of 100 percent hydrogen or a denitriding hydrogen bearing atmosphere, conducting said anneal at a temperature of from about 1,900° F. to about 2,500° F., maintaining the dew point of said annealing atmosphere at a level such as to prevent the formation of iron oxide at the surfaces of said stock, and maintaining said stock at temperature for from about 24 hours to about 140 hours, whereby to produce a ferrous stock having a final sulfur content of about 0.004 percent or less and a final nitrogen content of 0.004 percent or less.

10. A method of producing high-purity ferrous stock from ingot iron having an initial manganese content up to about 0.06 percent, comprising the steps of reducing the thickness of said ingot iron to a final gauge of from about 0.025 inches to about 0.080 inches, descaling said ingot iron, applying to said ingot irons an annealing separator chosen from the class consisting of calcium oxide, magnesia, lime, dolomite and combinations thereof, annealing said ingot iron in an atmosphere of 100 percent hydrogen, or a hydrogen-bearing atmosphere having a nitrogen content such as to prevent nitrogen pickup by said stock, conducting said anneal at a temperature of from about 2,100° F. to about 2,200° F., maintaining the dew point of said annealing atmosphere at a level of 30° F. or less and maintaining said ingot iron at temperature for a time of from 24 hours to 140 hours whereby to produce a ferrous stock having a final sulfur content of about 0.004 percent or less.

11. A high-purity, hot rolled ferrous material having a sulfur content of up to about 0.004 percent, a nitrogen content of up to about 0.004 percent, a phosphorous content of up to about 0.005 percent, an oxygen content of up to about 0.070 percent and a carbon content of up to about 0.018 percent, produced by the process of claim 1.

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