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METHOD OF IMPROVING THE AGING CHARACTERISTICS OF STEEL

Paul Werthebach, Dortmund, and Willi Wrede, Dortmund-Kirchderne, Germany, assignors to Hoesch Aktiengesellschaft, Dortmund, Germany

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The present invention relates to a method of improving the aging characteristics of steel and, more particularly, the present invention is concerned with reducing the nitrogen content of elongated steel bodies of relatively small cross-sectional dimensions so as to improve the aging characteristics thereof.

One of the main causes of age deterioration of steel is the presence of nitrogen which is dissolved in the iron. The solubility of nitrogen in alpha iron at room temperature is relatively low, namely less than 0.001%. However, the solubility of nitrogen in iron increases with increasing temperatures so that, for instance, at a temperature of 590° C. up to 0.10% nitrogen may be dissolved in the iron, provided that the steel melt contains such relatively high proportion of nitrogen.

Conventional technical steel generally contains considerably smaller proportions of nitrogen. For instance basic Bessemer steel usually will contain between 0.06% and 0.015% nitrogen and open hearth steel between 0.003% and 0.008%. The temperature at which about 0.015% nitrogen may be dissolved in iron is in the neighborhood of 300° C., and about 0.003% nitrogen are soluble in iron at a temperature about 150° C.

When steel containing a certain percentage of nitrogen is heated to such temperature that part or all of the nitrogen will be dissolved within the alpha lattice of the iron, then, it should be expected that upon subsequent cooling of the steel, the nitrogen would again precipitate except for a very small residual proportion of about 0.001% which may remain in solution even at ambient temperature. However, the precipitation of nitrogen upon cooling of the steel is a very slow process. Even the longest cooling periods which conventionally may be maintained in the smelter and rolling mill installations are too short in order to again precipitate the nitrogen which had been dissolved in the iron at higher temperatures. Only during prolonged storage, slow precipitation of nitrogen in the form of iron nitride will take place and this precipitation of iron nitride will cause impairment of the mechanical properties of the steel and generally is described as aging deterioration or just as aging. It is known that the degree of aging deterioration depends primarily on the amount of nitrogen contained in the steel and, in view thereof, attempts have been made to reduce the nitrogen content of the steel, preferably already during the smelting of the same. This, namely the intended reduction in the nitrogen content of the steel, is one of the reasons why it is more and more frequently attempted to blow pure oxygen gas in place of air during the conversion of pig iron into steel.

It has been found that it is also possible to reduce the nitrogen content of the finished steel product or steel body, provided that a cross-sectional dimension of the steel body is relatively small. Reduction in the nitrogen content of such steel bodies can be achieved by heating or annealing the steel body in an atmosphere including a large proportion of hydrogen gas. Apparently favored by the catalytic effect of a small proportion of steam, i.e. vaporized water, hydrogen will diffuse into the steel and will combine with the nitrogen dissolved therein under formation of ammonia. The ammonia will escape from the steel and immediately will be diluted and distributed in the surrounding protective gas atmosphere, provided that sufficient circulation of the gas atmosphere is maintained and fresh protective gas is admixed in sufficient proportions to maintain the atmosphere in which the steel body is exposed to annealing substantially free of ammonia.

The above method, as well as the improvement thereof in accordance with the present invention which will be described further below, is applicable to all types of steel with the exception of such steel which includes a metal having a high affinity to nitrogen. Thus, the present invention is primarily applicable to unalloyed steel and generally to all types of steel with the exception of steel containing 0.02% or more of aluminum. Generally, removal of nitrogen according to the present invention is still possible with steel containing up to 0.01% aluminum and such steel containing not more than about 0.01% aluminum will be called herein "substantially aluminum-free steel."

While there are limitations, in fact severe limitations, with respect to the aluminum content of steel which is to be treated according to the present invention, it is possible to treat in accordance with the present invention steel containing relatively large proportions of silicon, even containing 2% of silicon or more, by annealing such steel in a hydrogen gas-containing atmosphere.

For annealing of steel in gas mixtures including hydrogen gas, it is desirable that the hydrogen gas contacts substantially the entire surface of the steel body and that the thickness of the steel bodies is within certain limitations so that the treatment will affect not only the surface portion but the entire steel body.

In the case of steel strip or wire, this can be easily accomplished by uncoiling the steel strip or wire and passing it suspended through a continuous-type or tunnel furnace. However, particularly with respect to steel strip it is also possible to form loose coils of the same so that between adjacent coils there will be a distance of several millimeters which can be penetrated by the circulating hydrogen-containing atmosphere during annealing of the loose coil.

However, annealing as described above, namely in a somewhat moist, i.e. steam-containing, atmosphere which includes a major proportion of hydrogen gas and at relatively high temperatures, generally will also cause partial or complete decarbonization of the steel. Such decarbonization will occur even if the protective gas atmosphere contains only a very small proportion of steam. At conventional annealing temperatures, apparently, steam is decomposed into hydrogen and oxygen, and the free oxygen will oxidize the carbon located in the surface of the steel body under formation of carbon monoxide which is then removed by the circulating protective gas atmosphere. Carbon from the interior portion of the steel body will then diffuse into the surface portion thereof and again will react with oxygen, until a nearly complete decarbonization has taken place. Such decarbonization may be desirable in the case of very soft strips and wires, however, decarbonization of the steel is most undesirable in those cases where the steel must have a certain, relatively high degree of mechanical strength, for instance in the case of steel used for baling straps, spring strip, conveyor bands, wire ropes and the like, in which the hardness and the mechanical strength is strongly dependent on the carbon content. However, reduction of the nitrogen content of the last mentioned types of steel bodies is frequently of great importance in order to avoid increase in the brittleness thereof during aging. In view thereof, it has been proposed to first subject such steel bodies to annealing in an atmosphere containing a relatively large proportion of hydrogen gas, and thereafter to restore the lost carbon by further annealing of the steel body in a carbon-supplying medium. Obviously, to proceed in this manner is uneconomical and time consuming.

It is therefore an object of the present invention to overcome the above discussed difficulties in the reduction of the nitrogen content of steel bodies.

It is another object of the present invention to provide a method which will permit reducing the nitrogen content of steel bodies substantially without affecting the carbon content thereof.

It is yet another object of the present invention to provide a method for reducing the nitrogen content of steel bodies which method can be carried out in a simple and economical manner.

Other objects and advantages of the present invention will become apparent from a further reading of the description and of the appended claims.

With the above and other objects in view, the present invention contemplates a method of improving the aging characteristics of substantially aluminum-free steel, comprising the step of subjecting the steel in an atmosphere consisting essentially of nitrogen, hydrogen and steam to a heat treatment at a temperature between a first temperature being the temperature of incipient decarbonization of the steel and a second temperature being 100° C. lower than the first temperature and for a period of time sufficient to substantially reduce the nitrogen content of the steel, whereby the aging characteristics of the steel are improved due to reduction of the nitrogen content thereof without substantially affecting the carbon content of the steel.

In a preferred manner of improving the aging characteristics of an elongated substantially aluminum-free steel body having a maximum cross-sectional dimension of about 4 mm., the method of the present invention comprises the step of subjecting the steel body in an atmosphere consisting essentially of between 75% and 80% by volume of hydrogen gas, between 5% and 0.5% by volume of steam, the balance being nitrogen to a heat treatment within a temperature range of between about 500 to 600° C. and for a period of time sufficient to substantially reduce the nitrogen content of the steel, whereby the aging characteristics of the steel body are improved due to reduction of the nitrogen content thereof without substantially affecting the carbon content of the steel body.

Thus, according to the present invention, the nitrogen content of steel bodies, particularly steel bands and strips having a thickness of up to about 3 mm. and steel wire having a diameter of up to about 4 mm., is reduced by annealing the steel body (which should be substantially free of aluminum) in an atmosphere consisting of nitrogen, hydrogen and steam, within a temperature range such that the annealing temperature is not higher than the lowest temperature at which appreciable decarbonization of the steel will take place and not more than about 100° C. lower than such temperature of incipient decarbonization. Particularly in the case of conventional unalloyed steel, this temperature range will correspond to between about 500 and 600° C.

It is thus possible, according to the present invention, in a single annealing process, to reduce the nitrogen content of the steel strip or wire without, however, substantially affecting the carbon content of the steel.

Table I below illustrates the reduction in carbon and nitrogen content of basic Bessemer steel and open hearth steel upon annealing at various temperatures in a protective gas atmosphere consisting of 78% hydrogen, 2% steam, the balance being nitrogen:

Table I

UNKILLED BASIC BESSEMER STEEL STRIP 0.9 MM. THICKNESS

	° C.	Percent C	Percent N_2
Prior to annealing	----------	0.11	0.010
After annealing at	530	0.11	0.007
Do	560	0.11	0.002
Do	590	0.11	0.001
Do	620	0.09	0.001
Do	650	0.06	0.001
Do	700	0.01	0.001
Do	750	0.01	0.001

UNKILLED OPEN HEARTH STEEL STRIP 0.8 MM. THICKNESS

	° C.	Percent C	Percent N_2
Prior to annealing	----------	0.05	0.004
After annealing at	530	0.05	0.003
Do	560	0.05	0.001
Do	590	0.05	0.001
Do	620	0.03	0.001
Do	650	0.01	0.001
Do	750	0.01	0.001

The length of time for which annealing is to be carried out, under otherwise equal conditions, in order to reduce the nitrogen content of the above described basic Bessemer steel at a temperature of 590° C., depends on the concentration of hydrogen in the protective gas. At a hydrogen concentration approaching 100%, only 4 hours will be required. On the other hand, if the hydrogen concentration in the protective gas is reduced, the annealing time will be prolonged, for instance, at a hydrogen concentration of 60%, to 8 hours; at a hydrogen concentration of 40%, to 17 hours; and at a hydrogen concentration of 30%, to 22 hours.

Thus, while it is technically possible, it is impractical and uneconomical to anneal in a protective gas atmosphere which contains less than 40% hydrogen, and preferably the protective gas atmosphere should contain at least 50% hydrogen, while best results usually are achieved with even higher concentrations of hydrogen gas.

It is clearly apparent from Table I that decarbonization of the steel will take place only at temperatures higher than 590° C., while the nitrogen content of the steel will be greatly reduced already at temperatures such as 530° C. and nitrogen will be practically completely removed at about 590° C., since the residual proportion of nitrogen being only of the magnitude of 0.001% is without practical importance. It follows from Table I that the temperature range starting below the temperature at which substantial decarbonization of the steel will take place and reaching to about 100° below such incipient decarbonization temperature, will be the temperature range within which it is possible, in accordance with the present invention, to reduce the nitrogen content of the steel without appreciably influencing the carbon content thereof.

When it is desired to reduce the nitrogen content of heavily alloyed steel in accordance with the above described method of the present invention, then it will be frequently desirable first to determine experimentally the lowest temperature at which decarbonization will take place and, in accordance with such findings, to prescribe the desired annealing temperature or temperature range, which will be between such temperature of incipient decarbonization and a temperature which is about 100° C. lower than the incipient decarbonization temperature.

Broadly, the protective gas atmosphere under which annealing is carried out in accordance with the present invention in the indicated temperature range, will contain between 40 and 99.5% by volume of hydrogen gas, preferably between 68 and 89% and most preferably between 75 and 80%.

The steam content of the protective gas atmosphere should not exceed 5% by volume and broadly will be between 5 and about 0.5%, preferably between 1 and 2%; while the nitrogen content broadly should be maintained between 59.5 and 0% and preferably between 10 and 30%.

Very good results are obtained with a protective gas atmosphere containing 75% hydrogen, a small proportion of steam as indicated above, the balance being nitrogen. The proportion of hydrogen and nitrogen in such mixture will be approximately the same as is obtained upon decomposition of ammonia. The hydrogen content can also be increased up to close to 100%, however, for economical reasons as indicated above, namely in order not to unduly lengthen the process, preferably the hydrogen content will not be reduced to less than about 50% and, as stated above, the balance will primarily consist of nitrogen. Steam which will be contained in the protective atmosphere should be maintained at a low percentage, preferably not more than 2% and in any event not more than 5%, since, under certain conditions, larger steam concentrations might favor a decarbonization of the steel.

Theoretically the protective gas atmosphere may contain up to 100% hydrogen with traces of steam, however an increase of the hydrogen content beyond 80% doesn't give an acceleration or an improvement of the reduction of the nitrogen content in the steel. Therefore the protective gas atmosphere can obtain an additional, non-decarbonizing gas, i.e., non-oxidizing gas or rare gas. Most economical is the use of nitrogen as additional, non-decarbonizing gas but rare gas for instance argon may be used, too. Moreover the addition of non-oxidizing or rare gas to the protective gas atmosphere reduces the danger of gas explosion and therefore is opportune for security. Apparently the use of nitrogen as additional, non-carbonizing gas also seems to be advantageous because of a catalytic effect by primary formation of ammonia.

Compositions of protective gas atmospheres according to the present invention are summarized in Table II.

Table II

PROTECTIVE GAS COMPOSITION

	Maximum, percent	Preferred, percent	Minimum, percent
H_2	99.5	68-89	40
N_2	59.5	10-30	0
H_2O	5	1-2	0.5

Table III shows 5 preferred compositions of the protective gas or atmosphere:

Table III

Composition	I	II	III	IV	V
	Percent	*Percent*	*Percent*	*Percent*	*Percent*
H_2	75	78	79	85	90
N_2	23.5	20	19	14	8
H_2O	1.5	2	2	1	2

The following examples are given as illustrative only of the present invention without, however, limiting the invention to the specific details of the examples.

EXAMPLE I

A steel strip consisting of unkilled soft basic Bessemer steel of the following analysis: 0.11% C. 0.01% Si, 0.36% Mn, 0.045% P, 0.022% S and 0.010% N, and which had been cold rolled down to a thickness of 0.9 mm. was annealed for 5 hours, suspended in a protective gas atmosphere composed of 78% hydrogen, 20% nitrogen and 2% steam.

Depending on the annealing temperature, upon completion of the five hour annealing treatment, the carbon and nitrogen content of the steel strip was found to be as follows:

Annealing temperature (° C.)	C, percent	N, percent
530	0.11	0.007
560	0.11	0.002
590	0.11	0.001
620	0.09	0.001
650	0.06	0.001
700	0.01	0.001
750	0.01	0.001

Similar treatment of the same type of steel strip, however, in a protective gas atmosphere consisting of 90% hydrogen, 8% nitrogen and 2% steam gave the following results:

Annealing temperature (° C.)	C, percent	N, percent
530	0.11	0.006
560	0.11	0.003
590	0.11	0.001
620	0.08	0.001
650	0.05	0.0005
700	0.01	0.0005
750	0.005	0.0005

It can be seen that in both cases annealing at a temperature of up to 590° C. (and probably even somewhat higher, but below 620° C.) caused the desired reduction in the nitrogen content without affecting the carbon content of the steel.

EXAMPLE II

A deep drawn strip of unkilled open hearth steel of the following analysis: 0.05% C, 0.01% Si, 0.32% Mn, 0.012% P, 0.018% S and 0.004% N, and which had been cold rolled down to a thickness of 0.8 mm. was annealed for 5 hours, suspended in a protective gas atmosphere composed of 78% hydrogen, 20% nitrogen and 2% steam.

Upon completion of the five hour annealing process, and depending on the annealing temperature, the carbon and nitrogen content was found to be as follows:

Annealing temperature (° C.)	C, percent	N, percent
530	0.05	0.003
560	0.05	0.001
590	0.05	0.001
620	0.03	0.001
650	0.01	0.001
750	0.01	0.001

Similar treatment of the same type of steel strip, however, in a protective gas atmosphere consisting of 60% hydrogen, 38% nitrogen and 2% steam, and extension of the annealing treatment to 10 hours gave the following results:

Annealing temperature (° C.)	C, percent	N, percent
530	0.05	0.003
560	0.05	0.002
590	0.05	0.001
620	0.04	0.001
650	0.01	0.0005

Here again, annealing at a temperature of up to 590° C., resulted in the desired reduction of the nitrogen content without reducing the carbon content of the steel. However, in view of the lower hydrogen content of the protective gas atmosphere applied in the second test, the annealing time had to be prolonged.

EXAMPLE III

A strip of unkilled open hearth steel having a tensile strength of 37 kg./mm.^{2} and the following analysis: 0.16% C, 0.01% Si, 0.34% Mn, 0.015% P, 0.028% S and 0.005% N, and which has been cold rolled down to a thickness of 0.75 mm., was annealed in open-coil condition for 25 hours at a temperature of 630° C., in a protective gas atmosphere consisting of 79% hydrogen, 19% nitrogen and 2% steam.

Upon completion of the annealing treatment, it was found that the nitrogen content had been reduced to 0.0005% while the carbon content had only been slightly reduced to 0.14%. Thus, the strip had been substantially completely freed of nitrogen with only a relatively insignificant reduction in its carbon content.

EXAMPLE IV

A steel wire of electro furnace quality, destined to be incorporated in a wire rope and having the following analysis: 0.52% C, 0.22% Si, 0.60% Mn, 0.010% P, 0.008% S and 0.007% N was drawn to a diameter of 0.7 mm. and thereafter annealed for 4 hours at various temperatures while being suspended in a protective gas atmosphere consisting of 85% hydrogen, 14.7% nitrogen and 0.3% steam. Depending on the annealing temperature, the following carbon and nitrogen contents were found in the steel wire after completion of the four hour annealing treatment:

Annealing temperature (° C.)	C, percent	N, percent
500	0.51	0.006
540	0.50	0.004
580	0.50	0.001
620	0.48	0.0005
660	0.42	0.0005

It is noted that all percentage figures relating to the composition of the protective gas are given in percent by volume.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A method of improving the aging characteristics of substantially aluminum-free steel, comprising the step of subjecting steel containing up to 0.01% aluminum and more than 0.001% nitrogen in an atmosphere consisting essentially of between 40% and 95.5% by volume of hydrogen gas, between 5% and 0.5% by volume of steam and up to 59.5% by volume of at least one gas selected from the group consisting of nitrogen gas and rare gases to a heat treatment at a temperature between a first temperature being the temperature of incipient decarbonization of said steel and a second temperature being 100° C.

lower than said first temperature and for a period of time sufficient to substantially reduce the nitrogen content of said steel, whereby the aging characteristics of said steel are improved due to reduction of the nitrogen content thereof without substantially affecting the carbon content of said steel.

2. A method of improving the aging characteristics of an elongated substantially aluminum-free steel body having a maximum thickness of up to about 4 millimeters and containing up to 0.01% aluminum and more than 0.001% nitrogen, comprising the step of subjecting said steel body in an atmosphere consisting essentially of between 40% and 95.5% by volume of hydrogen gas, between 5% and 0.5% by volume of steam and up to 59.5% by volume of at least one gas selected from the group consisting of nitrogen gas and rare gases to a heat treatment at a temperature between a first temperature being the temperature of incipient decarbonization of said steel and a second temperature being 100° C. lower than said first temperature and for a period of time sufficient to substantially reduce the nitrogen content of said steel, whereby the aging characteristics of said steel body are improved due to reduction of the nitrogen content thereof without substantially affecting the carbon content of said steel body.

3. A method of improving the aging characteristics of an elongated substantially aluminum-free unalloyed steel body having a maximum thickness of up to about 4 millimeters and containing up to 0.01% aluminum and more than 0.001% nitrogen, comprising the step of subjecting said steel body in an atmosphere consisting essentially of between 40% and 95.5% by volume of hydrogen gas, between 5% and 0.5% by volume of steam and up to 59.5% by volume of at least one gas selected from the group consisting of nitrogen gas and rare gases to a heat treatment within a temperature range of between about 500 and 600° C. and for a period of time sufficient to substantially reduce the nitrogen content of said steel, whereby the aging characteristics of said steel body are improved due to reduction of the nitrogen content thereof without substantially affecting the carbon content of said steel body.

4. A method of improving the aging characteristics of an elongated substantially aluminum-free steel body having a maximum thickness of up to about 4 millimeters and containing up to 0.01% aluminum and more than 0.001% nitrogen, comprising the step of subjecting said steel body in an atmosphere consisting essentially of between 68% and 89% by volume of hydrogen gas, between 10% and 30% by volume of nitrogen gas and between 1% and 2% by volume of steam to a heat treatment within a temperature range of between about 500 and 600° C. and for a period of time sufficient to substantially reduce the nitrogen content of said steel, whereby the aging characteristics of said steel body are improved due to reduction of the nitrogen content thereof without substantially affecting the carbon content of said steel body.

5. A method of improving the aging characteristics of an elongated substantially aluminum-free steel body having a maximum thickness of up to about 4 millimeters and containing up to 0.01% aluminum and more than 0.001% nitrogen, comprising the step of subjecting said steel body in an atmosphere consisting essentially of between 75% and 80% by volume of hydrogen gas, between 5% and 0.5% by volume of steam, the balance being nitrogen, to a heat treatment within a temperature range of between about 500 and 600° C. and for a period of time sufficient to substantially reduce the nitrogen content of said steel, whereby the aging characteristics of said steel body are improved due to reduction of the nitrogen content thereof without substantially affecting the carbon content of said steel body.

6. A method of improving the aging characteristics of steel, comprising the step of subjecting steel containing up to 0.01% aluminum and more than 0.001% nitrogen in an atmosphere consisting of between 40% and 95.5% by volume of hydrogen gas, between 5% and 0.5% by volume of steam and up to 59.5% by volume of at least one gas selected from the group consisting of nitrogen gas and rare gases to a heat treatment at a temperature sufficiently high to reduce the nitrogen content of said steel, said temperature being below the temperature at which substantial decarbonization of said steel occurs.

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