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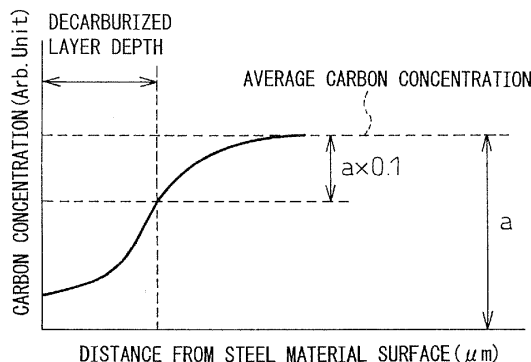
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(54) **HIGH-STRENGTH STEEL AND HIGH-STRENGTH BOLT WITH EXCELLENT RESISTANCE TO DELAYED FRACTURE, AND MANUFACTURING METHOD THEREFOR**

(57) A high strength steel material which is excellent in delayed fracture resistance containing, by mass%, C: 0.10 to 0.55%, Si: 0.01 to 3%, and Mn: 0.1 to 2%, further containing one or both of V: 1.5% or less and Mo: 3.0% or less, the contents of V and Mo satisfying $V+1/2Mo>0.4\%$, further containing one or more of Cr: 0.05 to 1.5%, Nb: 0.001 to 0.05%, Cu: 0.01 to 4%, Ni: 0.01 to 4%, and B: 0.0001 to 0.005%, and having a balance of Fe and unavoidable impurities, the structure being a mainly tempered martensite structure, the surface

of the steel material being formed with (a) a nitrided layer having a thickness from the surface of the steel material of 200 μm or more and a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material by 0.02 mass% or more and (b) a low carbon region having a depth from the surface of the steel material of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of the steel material.

Fig.2



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Description

Technical Field

5 **[0001]** The present invention relates to a high strength steel material which is used for wire rods, PC steel bars (steel bars for prestressed concrete use), etc., more particularly relates to a high strength steel material and high strength bolts of a tensile strength of 1300 MPa or more which are excellent in delayed fracture resistance and methods for the production of the same.

10 Background Art

[0002] The high strength steel which is used in large amounts for machines, automobiles, bridges, and building structures is medium carbon steel with an amount of C of 0.20 to 0.35%, for example, SCr, SCM, etc. defined by JIS G 4104 and JIS G 4105 which is quenched and tempered. However, in all types of steels, if the tensile strength exceeds 1300
15 MPa, the risk of delayed fracture occurring becomes larger.

[0003] As methods for improving the delayed fracture resistance of high strength steel, the method of making the steel structure a bainite structure or the method of refining the prior austenite grains is effective.

[0004] PLT 1 discloses steel which is refined in prior austenite grains and improved in delayed fracture resistance, while PLT's 2 and 3 disclose steels which suppress segregation of steel ingredients to improve the delayed fracture
20 resistance. However, with refinement of prior austenite grains or with suppression of segregation of ingredients, it is difficult to greatly improve the delayed fracture resistance.

[0005] A bainite structure contributes to improvement of the delayed fracture resistance, but formation of a bainite structure requires suitable additive elements or heat treatment, so the cost of the steel rises.

[0006] PLT's 4 to 6 disclose wire rods for high strength bolts containing 0.5 to 1.0 mass% of C in which an area ratio
25 80% or more of the pearlite structure is strongly drawn to impart 1200N/mm² or more strength and excellent delayed fracture resistance. However, the wire rods which are described in PLT's 4 to 6 are high in cost due to the drawing process. Further, manufacture of thick wire rods is difficult.

[0007] PLT 7 discloses a coil spring using oil-tempered wire of a hardness of the inside cross-section of Hv550 or more to suppress the occurrence of delayed fracture after cold coiling. However, the surface hardness of the product
30 after nitriding is Hv900 or more. Under high load stress such as with bolts or PC steel bars, the delayed fracture characteristics are low. If the corrosive environment becomes severer, there is the problem of delayed fracture occurring.

[0008] PLT 8 discloses a steel material which is excellent in delayed fracture resistance composed of steel of a required composition which is nitrided and mainly consists of a tempered martensite structure. The high strength steel material which is disclosed in PLT 8 exhibits delayed fracture resistance even under a corrosive environment containing hydrogen.

[0009] However, in recent years, corrosive environments have become harsher. A high strength steel material which
35 exhibits excellent delayed fracture resistance even under severe corrosive environments has been sought.

Citations List

40 Patent Literature

[0010]

PLT 1: JP-B2-64-4566
45 PLT 2: JP-A-3-243744
PLT 3: JP-A-3-243745
PLT 4: JP-A-2000-337332
PLT 5: JP-A-2000-337333
PLT 6: JP-A-2000-337334
50 PLT 7: JP-A-10-251803
PLT 8: JP-A-2009-299180

Summary of Invention

55 Technical Problem

[0011] As explained above, in high strength steel materials, there is a limit to improving the delayed fracture resistance by conventional methods. As a method for improving the delayed fracture resistance, there is the method of causing

fine precipitates to diffuse in the steel material and trapping hydrogen by the precipitates. However, even if employing this method, it is difficult to effectively suppress delayed fracture when the amount of hydrogen which enters from the outside is large.

[0012] The present invention, in view of this current situation, has as its object to provide a high strength steel material (wire rod or PC steel bar) and high strength bolt which exhibit excellent delayed fracture resistance even under a severe corrosive environment and methods of production for producing these inexpensively.

Solution to Problem

[0013] The inventors engaged in intensive research on the techniques for solving the above problem. As a result, they learned that if (a) introducing into the steel material predetermined amounts of V and/or Mo - which form precipitates which trap hydrogen, (b) decarburizing and nitriding the surface of the steel material (b1) to form a low carbon region to suppress hardening and (b2) to form a nitrided layer to obstruct absorption of hydrogen, the delayed fracture resistance is remarkably improved.

[0014] The present invention was made based on the above discovery and has as its gist the following:

(1) A steel material which is excellent in delayed fracture resistance containing, by mass%, C: 0.10 to 0.55%, Si: 0.01 to 3%, and Mn: 0.1 to 2%, further containing one or both of V: 1.5% or less and Mo: 3.0% or less, the contents of V and Mo satisfying $V+1/2Mo>0.4\%$, further containing one or more of Cr: 0.05 to 1.5%, Nb: 0.001 to 0.05%, Cu: 0.01 to 4%, Ni: 0.01 to 4%, and B: 0.0001 to 0.005%, and having a balance of Fe and unavoidable impurities, the structure being a mainly tempered martensite structure, the surface of the steel material being formed with

(a) a nitrided layer having a thickness from the surface of the steel material of 200 μm or more and a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material by 0.02 mass% or more and

(b) a low carbon region having a depth from the surface of the steel material of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of the steel material.

(2) A steel material which is excellent in delayed fracture resistance as set forth in (1) characterized in that due to the presence of the nitrided layer and low carbon region, the amount of absorption of hydrogen in the steel material is 0.5 ppm or less and the critical diffusible hydrogen content of the steel material is 2.00 ppm or more.

(3) A steel material which is excellent in delayed fracture resistance as set forth in (1) or (2) further characterized in that the steel material contains, by mass%, one or more of Al: 0.003 to 0.1%, Ti: 0.003 to 0.05%, Mg: 0.0003 to 0.01%, Ca: 0.0003 to 0.01%, and Zr: 0.0003 to 0.01%.

(4) A steel material which is excellent in delayed fracture resistance as set forth in any one of (1) to (3) characterized in that the nitrided layer has a thickness of 1000 μm or less.

(5) A steel material which is excellent in delayed fracture resistance as set forth in any one of (1) to (4) characterized in that the tempered martensite has an area ratio of 85% or more.

(6) A steel material which is excellent in delayed fracture resistance as set forth in any one of (1) to (5) characterized in that the steel material has a compressive residual stress at the surface of 200 MPa or more.

(7) A steel material which is excellent in delayed fracture resistance as set forth in any one of (1) to (6) characterized in that the steel material has a tensile strength of 1300 MPa or more.

(8) A bolt which is excellent in delayed fracture resistance obtained by working a steel material containing, by mass%, C: 0.10 to 0.55%, Si: 0.01 to 3%, and Mn: 0.1 to 2%, further containing one or both of V: 1.5% or less and Mo: 3.0% or less, the contents of V and Mo satisfying $V+1/2Mo>0.4\%$, further containing one or more of Cr: 0.05 to 1.5%, Nb: 0.001 to 0.05%, Cu: 0.01 to 4%, Ni: 0.01 to 4%, and B: 0.0001 to 0.005%, and having a balance of Fe and unavoidable impurities, the structure being a mainly tempered martensite structure, the surface of the bolt being formed with

(a) a nitrided layer having a thickness from the surface of the bolt of 200 μm or more and a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material by 0.02 mass% or more and

(b) a low carbon region having a depth from the surface of the bolt of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of the steel material.

(9) A high strength bolt which is excellent in delayed fracture resistance as set forth in (8) characterized in that due

to the presence of the nitrided layer and low carbon region, the amount of absorption of hydrogen in the bolt is 0.5 ppm or less and the critical diffusible hydrogen content of the bolt is 2.00 ppm or more.

(10) A high strength bolt which is excellent in delayed fracture resistance as set forth in (8) or (9) characterized in that the steel material further contains, by mass%, one or more of Al: 0.003 to 0.1%, Ti: 0.003 to 0.05%, Mg: 0.0003 to 0.01%, Ca: 0.0003 to 0.01%, and Zr: 0.0003 to 0.01%.

(11) A high strength bolt which is excellent in delayed fracture resistance as set forth in any one of (8) to (10) characterized in that the nitrided layer has a thickness of 1000 μm or less.

(12) A high strength bolt which is excellent in delayed fracture resistance as set forth in any one of (8) to (11) characterized in that the tempered martensite has an area ratio of 85% or more.

(13) A high strength bolt which is excellent in delayed fracture resistance as set forth in any one of (8) to (12) characterized in that the bolt has a compressive residual stress at the surface of 200 MPa or more.

(14) A high strength bolt which is excellent in delayed fracture resistance as set forth in any one of (8) to (13) characterized in that the bolt has a tensile strength of 1300 MPa or more.

(15) A method of production of a high strength steel material which is excellent in delayed fracture resistance as set forth in any one of (1) to (7),

the method of production of a high strength steel material which is excellent in delayed fracture resistance characterized by

(1) heating a steel material having a composition as set forth in (1) or (3) to form a low carbon region having a depth from the surface of the steel material of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of the steel material, then cooling as it is to make the steel material structure a mainly martensite structure, then

(2) nitriding the steel material at over 500°C to 650°C or less to form on the surface of the steel material a nitrided layer having a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material by 0.02 mass% and having a thickness from the surface of the steel material of 200 μm or more and to make the steel material structure a mainly tempered martensite structure.

(16) A method of production of a high strength steel material which is excellent in delayed fracture resistance as set forth in (15) characterized in that the nitrided layer has a thickness of 1000 μm or less.

(17) A method of production of a bolt which is excellent in delayed fracture resistance as set forth in any one of (8) to (14),

the method of production of a bolt which is excellent in delayed fracture resistance characterized by

(1) heating a bolt obtained by working a steel material having a composition as set forth in (8) or (10) to form a low carbon region having a depth from the surface of the bolt of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of the steel material, then cooling as it is to make the steel material structure a mainly martensite structure, then

(2) nitriding the bolt at over 500°C to 650°C or less to form on the surface of the bolt a nitrided layer having a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material by 0.02 mass% and having a thickness from the surface of the bolt of 200 μm or more and to make the steel material structure a mainly tempered martensite structure.

(18) A method of production of a bolt which is excellent in delayed fracture resistance as set forth in (17), characterized in that the nitrided layer has a thickness of 1000 μm or less.

Advantageous Effect of Invention

[0015] According to the present invention, it is possible to provide a high strength steel material (wire rod or PC steel bar) and high strength bolt which exhibit excellent delayed fracture resistance even in a severe corrosive environment and methods for production able to produce these inexpensively.

Brief Description of Drawings

[0016]

FIG. 1(a) is a view which schematically shows a hydrogen evolution rate curve which is obtained by hydrogen analysis by the thermal desorption analysis.

FIG. 1(b) is a view which schematically shows the relationship between a fracture time obtained by a constant load delayed fracture test of a steel material and an amount of diffusible hydrogen.

FIG. 2 is a view which shows a method of finding a depth (thickness) of a low carbon region from a carbon concentration

curve which is obtained by an Energy Dispersion type X-ray Spectrometer (EDX).

FIG. 3 is a view which shows a method of finding a thickness (depth) of a nitrated region from a nitrogen concentration curve which is obtained by an Energy Dispersion type X-ray Spectrometer (EDX).

FIG. 4 is a view which shows a test piece which is used for a delayed fracture test of a steel material.

FIG. 5 is a view which shows one mode of a delayed fracture test machine.

FIG. 6 is a view which shows a relationship between temperature and humidity in an accelerated corrosion test and time.

Description of Embodiments

[0017] It is known that hydrogen in steel causes delayed fracture. Further, absorption of hydrogen into the steel occurs along with corrosion in actual environments. The ingress of diffusible hydrogen into the steel concentrates at the concentrated parts of tensile stress and results in occurrence of delayed fracture.

[0018] FIG. 1(a) schematically shows a hydrogen evolution rate curve obtained by hydrogen analysis by the thermal desorption analysis. As shown in FIG. 1(a), the amount of release of diffusible hydrogen reaches a peak near 100°C.

[0019] In the present invention, a sample is raised in temperature by 100°C/h and the cumulative value of the amount of hydrogen which is released from room temperature to 400°C is defined as the amount of diffusible hydrogen. Note that, the amount of released hydrogen can be measured by a gas chromatograph.

[0020] In the present invention, the minimum amount of diffusible hydrogen at which delayed fracture occurs is referred to as the "critical diffusible hydrogen content". The limit amount of diffusible hydrogen differs according to the type of the steel.

[0021] FIG. 1(b) schematically shows the relationship between the fracture time obtained by a constant load delayed fracture test of the steel material and the amount of diffusible hydrogen. As shown in FIG. 1(b), if the amount of diffusible hydrogen is great, the fracture time is short, while if the amount of diffusible hydrogen is small, the fracture time is long.

[0022] That is, if the amount of diffusible hydrogen is small, delayed fracture does not occur, while if the amount of diffusible hydrogen is great, delayed fracture occurs. In the present invention, a constant load delayed fracture test of the steel material is run and, as shown in FIG. 1(b), the maximum value of the amount of diffusible hydrogen at which no fracture occurs for 100 hours or more was made the critical diffusible hydrogen content.

[0023] If comparing the amount of absorption of hydrogen and the critical diffusible hydrogen content and if the critical diffusible hydrogen content is greater than the amount of absorption of hydrogen, delayed fracture does not occur. Conversely if the critical diffusible hydrogen content is smaller than the amount of absorption of hydrogen, delayed fracture occurs. Therefore, the larger the critical diffusible hydrogen content, the more the occurrence of delayed fracture is suppressed.

[0024] However, if the amount of absorption of hydrogen in the steel material from a corrosive environment exceeds the critical diffusible hydrogen content, delayed fracture occurs.

[0025] Therefore, to prevent the occurrence of delayed fracture, it is effective to suppress absorption of hydrogen into the steel material. For example, if forming a nitrated layer at the surface of the steel material by nitriding, the amount of absorption of hydrogen due to corrosion is suppressed, so the delayed fracture resistance is improved.

[0026] However, if forming a nitrated layer at the steel material surface, due to hardening of the surface layer, the critical diffusible hydrogen content decreases and the delayed fracture resistance is not improved. Therefore, the inventors studied the composition of the steel material predicated on trapping and rendering harmless the hydrogen due to ingress in the steel material by fine precipitates so as to increase the critical diffusible hydrogen content.

[0027] As a result, the inventors confirmed that if including suitable amounts of one or both of V and Mo and causing fine precipitates composed of carbides, nitrides, and/or carbonitrides of V or Mo to form in the steel material, it is possible to increase the critical diffusible hydrogen content.

[0028] However, on the other hand, it was confirmed that even if the steel material is made to contain one or both of V and Mo, sometimes improvement of the delayed fracture resistance cannot be sufficiently obtained.

[0029] Therefore, the inventors engaged in repeated intensive studies focusing on the relationship between the crystal structure of the fine precipitates and the critical diffusible hydrogen content and amount of absorption of hydrogen and as a result learned the following.

[0030] The hexagonal carbides, nitrides, and carbonitrides of Mo have a larger effect of increase of the critical diffusible hydrogen content than the effect of increase of the amount of absorption of hydrogen, so contribute to the improvement of the delayed fracture resistance, but compared with the NaCl-type structures of carbides, nitrides, and carbonitrides of V, the effect of improvement of strength by fine precipitation is small.

[0031] On the other hand, NaCl-type structures of carbides, nitrides, and carbonitrides of V are excellent in the effect of improvement of strength due to fine precipitation. However, the NaCl-type structures of carbides, nitrides, and carbonitrides of V increase the critical diffusible hydrogen content, while also increase the amount of absorption of hydrogen, so the effect of improvement of the delayed fracture resistance is smaller compared with the hexagonal carbides, nitrides,

and carbonitrides of Mo.

[0032] That is, in a steel material, to secure the required strength and secure excellent delayed fracture resistance, it is necessary to suitably set the contents of Mo and V.

[0033] Therefore, the inventors engaged in in-depth studies to suitably set the contents of Mo and V. As a result, they learned that if including one or both of V: 1.5 mass% or less and Mo: 3.0 mass% or less and making the contents of V and Mo (mass%) satisfy $V+1/2Mo>0.4$ mass%, the critical diffusible hydrogen content is increased and an excellent delayed fracture resistance is obtained.

[0034] Further, the inventors studied lowering the hardness of the nitrided layer to improve the delayed fracture resistance, carried out accelerated corrosion tests and exposure tests on steel materials which were decarburized on the surface and, furthermore, nitrided, and investigated the hydrogen ingress characteristics and delayed fracture resistance of the steel material.

[0035] As a result, the inventors learned that if forming a nitrided layer of a predetermined nitrogen concentration and thickness on the surface of a steel material which has a predetermined composition and structure and, furthermore, forming a low carbon region of a predetermined carbon concentration and depth on the steel material surface, the delayed fracture resistance is remarkably improved compared with the case of forming only a nitrided layer on the steel material surface.

[0036] This is believed to be due to the synergistic effect of (1) suppression of the amount of absorption of hydrogen compared with the case of a nitrided layer alone due to the formation of a nitrided layer at the low carbon region which is formed at the steel material surface and (2) suppression of excessive hardening of the surface and increase of the critical diffusible hydrogen content due to the formation of the low carbon region at the steel material surface.

[0037] Basically, they learned that if forming, on the surface of a steel material of a predetermined composition and structure, (a) a nitrided layer having a thickness from the surface of the steel material of 200 μm or more and a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material by 0.02 mass% or more and (b) a low carbon region having a depth from the surface of the steel material of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of the steel material, it is possible to increase the critical diffusible hydrogen content of the steel material and reduce the amount of absorption of hydrogen.

[0038] Further, the inventors discovered that by heating and rapid cooling at the time of nitriding, compressive residual stress occurs at the steel material surface and the delayed fracture resistance is improved. In particular, in the case of a high strength bolt in which strain is introduced into the surface by working, formation of a nitrided layer is promoted. Further, the nitrogen concentration becomes higher, so the delayed fracture resistance is remarkably improved.

[0039] Below, the present invention will be explained in detail.

[0040] The high strength steel material and high strength bolt of the present invention are composed of predetermined compositions of ingredients and have a nitrided layer and a low carbon region simultaneously present on the surface.

[0041] That is, at the surface of the high strength steel material and high strength bolt of the present invention, there is a region with a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material by 0.02 mass% or more and with a carbon concentration of 0.05 mass% or more and 0.9 time or less the steel material (low carbon nitrided layer).

[0042] When the thickness of the nitrided layer is greater than the thickness of the low carbon region, the carbon concentration at the location deeper than the low carbon region is equal to the carbon concentration of the steel material and the nitrogen concentration is higher than the nitrogen concentration of the steel material.

[0043] On the other hand, when the thickness of the low carbon region is greater than the thickness of the nitrided layer, the result is a low carbon region with a carbon concentration of 0.05 mass% or more and 0.9 times or less of the carbon concentration of the steel material and with contents of other elements equal to the steel material is present under the nitrided layer.

[0044] First, the low carbon region will be explained. In the present invention, the low carbon region is a region with a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of the high strength steel material or high strength bolt.

[0045] In the high strength steel material and high strength bolt of the present invention, a low carbon region is formed at a depth of 100 μm or more to 1000 μm from the steel material surface.

[0046] The depth and carbon concentration of the low carbon region adjust the heating atmosphere, heating temperature, and holding time at the time of heat treatment which forms the low carbon region. For example, if the carbon potential of the heating atmosphere is low, the heating temperature is high, and the holding time is long, the low carbon region becomes deeper and the carbon concentration of the low carbon region falls.

[0047] If the carbon concentration of the low carbon region is less than 0.05 mass%, this becomes less than half of the lower limit 0.10 mass% of the carbon concentration of the steel material, so it is not possible to secure a predetermined strength and hardness by the low carbon region. If the carbon concentration of the low carbon region is over 0.9 time the carbon concentration of the steel material, this is substantially equal to the carbon concentration of the steel material

and the effect of presence of the low carbon region ends up becoming weaker.

[0048] For this reason, in the present invention, the low carbon region was defined as a region where the carbon concentration is 0.05 mass% or more and 0.9 time or less the carbon concentration of the steel material.

[0049] If the carbon concentration of the low carbon region is 0.05 mass% or more and 0.9 time or less of the carbon concentration of the steel material, it is possible to reduce the amount of increase in the surface hardness due to formation of the nitrided layer. As a result, the hardness of the surface of the steel material becomes equal to the hardness of the steel material or lower than the hardness of the steel material and can prevent a reduction of the critical diffusible hydrogen content.

[0050] The depth (thickness) of the low carbon region was made a depth (thickness) of 100 μm or more from the surface of the steel material or bolt so that the effect is obtained. The depth (thickness) of the low carbon region is preferably greater in depth (thickness), but if over 1000 μm , the strength of the steel material as a whole or the bolt as a whole falls, so the depth (thickness) of the low carbon region is given an upper limit of 1000 μm .

[0051] Next, a nitrided layer will be explained. In the present invention, the nitrided layer is a region with a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material or bolt by 0.02 mass% or more. Further, the nitrided layer is formed by a thickness of 200 μm or more from the surface of the steel material or bolt.

[0052] The thickness and nitrogen concentration of the nitrided layer can be adjusted by the heating atmosphere, heating temperature, and holding time at the time of nitriding. For example, if the concentration of ammonia or nitrogen in the heating atmosphere is high, the heating temperature is high, and the holding time is long, the nitrided layer becomes thicker and the nitrogen concentration of the nitrided layer becomes higher.

[0053] If the nitrogen concentration of the nitrided layer is higher than the nitrogen concentration of the steel material, it is possible to reduce the amount of absorption of hydrogen in the steel material from a corrosive environment, but if the difference of the nitrogen concentration of the nitrided layer and the nitrogen concentration of the steel material is less than 0.02 mass%, the effect of reduction of the amount of absorption of hydrogen cannot be sufficiently obtained. For this reason, the nitrogen concentration of the nitrided layer was made a concentration higher than the nitrogen concentration of the steel material by 0.02 mass% or more.

[0054] On the other hand, if the nitrogen concentration exceeds 12.0 mass%, the nitrided layer excessively rises in hardness and becomes brittle, so 12.0 mass% was made the upper limit.

[0055] If the steel material surface is formed with a nitrided layer which has a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of the steel material by 0.02 mass% or more and a depth of 200 μm or more from the surface, the amount of absorption of hydrogen in the steel material from the corrosive environment is greatly reduced.

[0056] The nitrided layer was limited to a thickness (depth) of 200 μm or more from the surface of the steel material or bolt so that the effect is obtained. The upper limit of the thickness of the nitrided layer is not particularly defined, but if the thickness is over 1000 μm , the productivity falls and a rise in cost is invited, so 1000 μm or less is preferable.

[0057] The depth (thickness) of the low carbon region which is formed on the high strength steel material or high strength bolt of the present invention can be found from the curve of the carbon concentration from the surface of the steel material or bolt.

[0058] A cross-section of a steel material or bolt which has a low carbon region and nitrided layer on the surface is polished and an Energy Dispersive X-ray Spectroscopy (below, sometimes referred to as "EDX") or a Wavelength Dispersive X-ray Spectroscopy (below, sometimes referred to as "WDS") is used for line analysis to measure the carbon concentration in a depth direction from the surface.

[0059] FIG. 2 shows the method of finding the depth (thickness) of the low carbon region from the curve of the carbon concentration which is obtained by EDX. That is, FIG. 2 is a view which shows the relationship between the distance from the steel material surface, obtained by measuring the carbon concentration in the depth direction from the surface using EDX, and the carbon concentration.

[0060] As shown in FIG. 2, the carbon concentration increases along with the increased distance (depth) from the steel material surface. This is because due to decarburization, a low carbon region is formed on the surface of the steel material.

[0061] In the region not affected by the decarburization, the carbon concentration is substantially constant (average carbon concentration "a"). The average carbon concentration "a" is the carbon concentration of the region not affected by the decarburization and is equal to the amount of carbon of the steel material before decarburization.

[0062] Therefore, in the present invention, the chemical analysis value of the carbon concentration of the steel material is made the reference value when finding the depth of the low carbon region.

[0063] As shown in FIG. 2, it is possible to discriminate the range where the carbon concentration from the steel material surface to the required depth becomes lower than 10% or more of the average carbon concentration "a" ($a \times 0.1$) (range of 0.9 time or less of the carbon concentration of the steel material) and find the distance (depth) from the steel material surface at the boundary of that range in the depth direction so as to evaluate the depth (thickness) of the

low carbon region.

[0064] The thickness (depth) of the nitrided layer can be found from the change of the nitrogen concentration from the surface of the steel material or bolt in the same way as the low carbon region. Specifically, a cross-section of the steel material or bolt which has a low carbon region and nitrided layer on the surface is polished and an EDX or WDS is used for line analysis to measure the nitrogen concentration in the depth direction from the surface.

[0065] FIG. 3 shows the method of finding the thickness (depth) of the nitrided layer from the nitrogen concentration curve obtained by an Energy Dispersion type X-ray Spectrometer (EDX). That is, FIG. 3 is a view showing the relationship between the distance from the steel material surface and the nitrogen concentration which is obtained by measuring the nitrogen concentration in the depth direction from the surface using EDX.

[0066] As the distance (depth) from the steel material surface becomes longer, the nitrogen concentration decreases, but in the region not affected by nitriding, the carbon concentration is substantially constant (average nitrogen concentration).

[0067] The average nitrogen concentration is a range of nitrogen concentration not affected by nitriding and is equal to the amount of nitrogen of the steel material before nitriding. Therefore, in the present invention, the chemical analysis value of the nitrogen concentration of the steel material is made the reference value when finding the thickness of the nitrided layer.

[0068] As shown in FIG. 3, it is possible to discriminate the region in which the nitrogen concentration from the steel material surface down to the required depth becomes higher than the average nitrogen concentration by 0.02 mass% or more and finding the distance (depth) from the steel material surface at the boundary of that region in the depth direction so as to evaluate the thickness (depth) of the nitrided layer.

[0069] The depth of the low carbon region and the thickness of the nitrided layer are found by obtaining simple averages of the values which were measured at any five locations at the cross-section of the steel material or bolt.

[0070] Note that, the carbon concentration and nitrogen concentration of the steel material may be found by measuring the carbon concentration and nitrogen concentration at a position sufficiently deeper than the depth of the low carbon region and nitrided layer, for example, a position at a depth of 2000 μm or more from the surface. Further, it is also possible to obtain an analytical sample from a position at a depth of 2000 μm or more from the surface of the steel material or bolt and chemically analyze it to find them.

[0071] In the high strength steel material of the present invention, as explained above, the delayed fracture is remarkably improved by the synergistic effect of (1) suppression of the amount of absorption of hydrogen due to the formation of a nitrided layer at the low carbon region which is formed at the steel material surface and (2) increase of the critical diffusible hydrogen content due to the formation of the low carbon region at the steel material surface.

[0072] According to investigations by the inventors, the surface of the steel material has a nitrided layer and a low carbon region copresent on it, whereby the amount of absorption of hydrogen in the steel material can be suppressed to 0.5 ppm or less and the critical diffusible hydrogen content of the steel material can be raised to 2.00 ppm or more.

[0073] Next, the reasons for limitation of the composition of the steel material will be explained. Below, the % according to the composition mean mass%.

[0074] C: C is an essential element in securing the strength of a steel material. If less than 0.10%, the required strength is not obtained, while if over 0.55%, the ductility and toughness fall and the delayed fracture resistance also falls, so the content of C was made 0.10 to 0.55%.

[0075] Si: Si is an element which improves strength by solution strengthening. If less than 0.01%, the effect of addition is insufficient, while if over 3%, the effect becomes saturated, so the content of Si was made 0.01 to 3%.

[0076] Mn: Mn is an element which not only performs deoxidation and desulfurization, but also gives a martensite structure, so lowers the transformation temperature of the pearlite structure or bainite structure to raise the hardenability. If less than 0.1%, the effect of addition is insufficient, while if over 2%, it segregates at the grain boundary at the time of heating of austenite to embrittle the grain boundary and degrades the delayed fracture resistance, so the content of Mn was made 0.1 to 2%.

[0077] The high strength steel material or high strength bolt of the present invention contains one or both of V and Mo to improve the delayed fracture resistance.

[0078] V: V is an element which causes the formation of fine precipitates of carbides, nitrides, and/or carbonitrides in the steel material. These fine precipitates act to trap and render harmless the hydrogen due to ingress in the steel material and increase the critical diffusible hydrogen content. Further, the fine precipitates contribute to the improvement of strength of the steel material.

[0079] Further, V is an element which lowers the transformation temperature of the pearlite structure or bainite structure and increases the hardenability and also raises the resistance to softening during tempering at the time of tempering to contribute to improvement of the strength.

[0080] If the content of V exceeds 1.5%, the solution temperature for precipitation strengthening becomes higher and, further, the ability for trapping hydrogen also becomes saturated, so the content was made 1.5% or less. If the content of V is less than 0.05%, an effect of improvement of strength due to the formation of fine precipitates is not sufficiently

obtained, so 0.05% or more is preferable.

[0081] Mo: Mo is an element which causes the formation of fine precipitates of carbides, nitrides, and/or carbonitrides in the steel material. The fine precipitates act to trap and render harmless the hydrogen due to ingress in the steel material and increase the critical diffusible hydrogen content. Further, fine precipitates contribute to an improvement of strength of the steel material and increases the critical diffusible hydrogen content to contribute to the improvement of the delayed fracture resistance.

[0082] Further, Mo is an element which lowers the transformation temperature of the pearlite structure or bainite structure to raise the hardenability and raises the resistance to softening during tempering at the time of tempering to contribute to the improvement of the strength.

[0083] If the content of Mo exceeds 3.0%, the solution temperature for precipitation strengthening becomes higher and, further, the ability for trapping hydrogen also becomes saturated, so the content was made 3.0% or less. If the content of Mo is less than 0.4%, an effect of increase of the critical diffusible hydrogen content due to the formation of fine precipitates is not sufficiently obtained, so 0.4% or more is preferable.

[0084] $V+1/2Mo$: In the present invention, the contents of Mo and V have to satisfy $V+1/2Mo>0.4\%$. If the contents of V and Mo satisfy this formula, the amount of V whereby not only the critical diffusible hydrogen content, but also the amount of absorption of hydrogen increases becomes relatively smaller than the amount of Mo, so the critical diffusible hydrogen content increases and an excellent delayed fracture resistance is obtained.

[0085] The high strength steel material or high strength bolt of the present invention may further contain one or more of Cr, Nb, Cu, Ni, and B in a range not impairing the excellent delayed fracture resistance for the purpose of improving the strength.

[0086] Cr: Cr is an element which lowers the transformation temperature of the pearlite structure or bainite structure to raise the hardenability and, further, raises the resistance to softening during tempering at the time of tempering to contribute to the improvement of the strength. If less than 0.05%, the effect of addition is not sufficiently obtained, while if over 1.5%, deterioration of the toughness is invited, so the content of Cr was made 0.05 to 1.5%.

[0087] Nb: Nb, like Cr, is an element which raises the hardenability and the tempering softening resistance to contribute to the improvement of the strength. If less than 0.001%, the effect of addition is not sufficiently obtained. If over 0.05%, the effect of addition becomes saturated, so the content of Nb was made 0.001 to 0.05%.

[0088] Cu: Cu is an element which contributes to the improvement of the hardenability, increase of the temper softening resistance, and improvement of strength by the precipitation effect. If less than 0.01%, the effect of addition is not sufficiently obtained, while if over 4%, grain boundary embrittlement occurs and the delayed fracture resistance deteriorates, so the content of Cu was made 0.01 to 4%.

[0089] Ni: Ni is an element which raises the hardenability and is effective for improvement of the ductility and toughness which fall along with increased strength. If less than 0.01%, the effect of addition is not sufficiently obtained, while if over 4%, the effect of addition becomes saturated, so the content of Ni was made 0.01 to 4%.

[0090] B: B is an element which suppresses grain boundary fracture and is effective for improvement of the delayed fracture resistance. Furthermore, B is an element which segregates at the austenite grain boundary and remarkably raises the hardenability. If less than 0.0001%, the effect of addition cannot be sufficiently obtained, while if over 0.005%, B carbides and Fe borocarbides form at the grain boundaries, grain boundary embrittlement occurs, and delayed fracture resistance falls, so the content of B is made 0.0001 to 0.005%.

[0091] The high strength steel material and high strength bolt of the present invention may further contain, for the purpose of refining the structure, one or more of Al, Ti, Mg, Ca, and Zr in a range not detracting from the excellent delayed fracture resistance.

[0092] Al: Al is an element which forms oxides or nitrides and prevents coarsening of austenite grains to suppress deterioration of the delayed fracture resistance. If less than 0.003%, the effect of addition is insufficient, while if over 0.1%, the effect of addition becomes saturated, so the content of Al is preferably 0.003 to 0.1%.

[0093] Ti: Ti also, like Al, is an element which forms oxides or nitrides to prevent coarsening of austenite grains and suppress deterioration of the delayed fracture resistance. If less than 0.003%, the effect of addition is insufficient, while if over 0.05%, the Ti carbonitrides coarsen at the time of rolling or working or at the time of heating in heat treatment and the toughness falls, so the content of Ti is preferably 0.003 to 0.05%.

[0094] Mg: Mg is an element which has a deoxidizing and desulfurizing effect and, further, forms Mg oxides, Mg sulfides, Mg-Al, Mg-Ti, and Mg-Al-Ti composite oxides or composite sulfides, etc. to prevent coarsening of austenite grains and suppress deterioration of delayed fracture resistance. If less than 0.0003%, the effect of addition is insufficient, while if over 0.01%, the effect of addition becomes saturated, so the content of Mg is preferably 0.0003 to 0.01%.

[0095] Ca: Ca is an element which has a deoxidizing and desulfurizing effect and, further, forms Ca oxides, Ca sulfides, Al, Ti, and Mg composite oxides or composite sulfides, etc. to prevent coarsening of austenite grains and suppress deterioration of delayed fracture resistance. If less than 0.0003%, the effect of addition is insufficient, while if over 0.01%, the effect of addition becomes saturated, so the content of Ca is preferably 0.0003 to 0.01%.

[0096] Zr: Zr is an element which forms Zr oxides, Zr sulfides, Al, Ti, Mg, and Zr composite oxides or composite

sulfides, etc. to prevent coarsening of austenite grains and suppress deterioration of delayed fracture resistance. If less than 0.0003%, the effect of addition is insufficient, while if over 0.01%, the effect of addition becomes saturated, so the content of Zr is preferably 0.0003 to 0.01%.

5 Steel Structure

[0097] Next, the structure of the high strength steel material and high strength bolt of the present invention (below, sometimes called "the steel structure of the present invention") will be explained. The steel structure of the present invention is mainly tempered martensite, so the structure is excellent in ductility and toughness even if the tensile strength is 1300 MPa or more.

[0098] The steel structure of the present invention is preferably a structure where the area ratio of the tempered martensite in the region excluding the low carbon region and nitrided layer is 85% or more and the balance is composed of one or more of residual austenite, bainite, pearlite, and ferrite.

[0099] The area ratio of the tempered martensite is measured at a deeper position between the depth at which the carbon concentration becomes constant in the carbon concentration curve which is shown in FIG. 2 and the depth where the nitrogen concentration becomes constant in the nitrogen concentration curve which is shown in FIG. 3.

[0100] For example, it is sufficient to measure the depth of 2000 μm or more from the surface of the steel material or bolt or the area ratio of the tempered martensite at locations of 1/4 of the thickness or diameter of the steel material.

[0101] Note that, the area ratio of martensite can be found by observing the cross-section of the steel material using an optical microscope and measuring the area of martensite per unit area. Specifically, the cross-section of the steel material is etched by a Nital etching solution, the areas of martensite in five fields in a range of 0.04 mm^2 are measured, and the average value is calculated.

[0102] Further, in the steel material of the present invention, compressive residual stress of the steel material surface occurs due to the heating and rapid cooling at the time of nitriding whereby the delayed fracture resistance is improved. If the compressive residual stress occurs by 200 MPa or more, the delayed fracture resistance is improved, so the compressive residual stress of the surface of the steel material of the present invention is preferably 200 MPa or more.

[0103] The compressive residual stress can be measured by X-ray diffraction. Specifically, the residual stress of the steel material surface is measured, then the steel material surface is etched 25 μm at a time by electrolytic polishing and the residual stress in the depth direction is measured. It is preferable to measure any three locations and use the average value of the same.

[0104] In a steel material in which no low carbon region and nitrided layer are formed on the surface, if the tensile strength becomes 1300 MPa or more, the frequency of occurrence of delayed fracture remarkably increases. Therefore, if the tensile strength is 1300 MPa or more, the delayed fracture resistance of the steel material of the present invention on which a low carbon region and nitrided layer are formed on the surface is remarkably excellent.

[0105] The upper limit of the tensile strength of the present invention is not particularly limited, but over 2200 MPa is technically difficult at the present point of time, so 2200 MPa is provisionally made the upper limit. Note that the tensile strength may be measured based on JIS Z 2241.

Method of Production

[0106] Next, a method of production of a steel material of the present invention will be explained.

[0107] The method of production of a steel material of the present invention is composed of a decarburization step of heating a steel material of a required composition (wire rod or PC steel bar or steel material worked to a predetermined shape) to decarburize it, a hardening step of cooling the decarburized steel material to make the steel structure a mainly martensite structure, and a step of nitriding the hardened steel material at over 500°C to 650°C or less.

[0108] Note that, due to the nitriding step, the structure of the steel material of the present invention becomes a structure of mainly tempered martensite.

[0109] In the decarburization step, the steel material of the present invention is decarburized to make the carbon concentration, down from the surface of the steel material by a depth of 100 μm or more to 1000 μm or less, 0.05% or more and 0.9 time or less the carbon concentration of the steel material. The atmosphere in the heating furnace is, for example, adjusted to a concentration of methane gas to make it weakly decarburizing and form a low carbon region.

[0110] The heating temperature in the decarburization is preferably A_{c3} to 950°C. By heating to A_{c3} or more, it is possible to make the steel structure austenite, promote decarburization from the surface layer, and easily form a low carbon region.

[0111] The upper limit of the heating temperature is preferably 950°C in the point that this suppresses coarsening of the crystal grains and improves the delayed fracture resistance. The holding time at the heating temperature is preferably 30 to 90 minutes. By holding at the heating temperature for 30 minutes or more, it is possible to sufficiently secure the depth of the low carbon region and possible to make the steel structure uniform. If considering the productivity, the

holding time at the heating temperature is preferably 90 minutes or less

[0112] At the hardening step, the heated steel material is cooled to obtain a mainly martensite structure. The heated steel material may be oil quenched as it is for hardening.

[0113] In the steel structure of the present invention, the area ratio of the tempered martensite is preferably 85% or more, so the area ratio of the martensite after hardening is preferably 85% or more.

[0114] At the hardening step, to secure an area ratio of the martensite of 85% or more, at the time of hardening, it is preferable to make the cooling rate in the range from 700 to 300°C 5°C/s or more. If the cooling rate is less than 5°C/s, sometimes the area ratio of the martensite becomes less than 85%.

[0115] At the nitriding step, a steel material with a steel structure of mainly martensite and formed with a low carbon region at the surface layer is nitrided. Due to the nitriding, a nitrided layer is formed with a thickness from the steel material surface of 200 μm or more and a nitrogen concentration of 12.0% or less and higher than the nitrogen concentration of the steel material by 0.02% or more. At the same time, the steel material is tempered to make the steel structure a mainly tempered martensite structure and to form fine precipitates which trap hydrogen.

[0116] In the method of production of a steel material of the present invention, the steel material contains one or both of V and Mo, so in the nitriding step, fine carbides, nitrides, and/or carbonitrides (fine precipitates) which act to trap the hydrogen are formed.

[0117] The nitriding is performed by, for example, heating the steel material in an atmosphere containing ammonia or nitrogen. The nitriding is preferably performed by holding the sample at over 500°C to 650°C or less for 30 to 90 minutes. If the nitriding temperature exceeds 650°C, the steel material falls in strength, so the nitriding temperature is made 650°C or less.

[0118] If the nitriding temperature is 500°C or less, fine precipitates do not sufficiently form, so the nitriding temperature is made over 500°C. Further, if the nitriding temperature is made over 500°C, the time required for diffusion of nitrogen from the steel material surface becomes shorter, the treatment time is shortened, and the productivity rises.

[0119] If the nitriding time is less than 30 minutes, the depth of the nitrided layer is liable not to reach a depth of 200 μm or more from the surface, so the nitriding time is preferably 30 minutes or more. The upper limit of the nitriding time is not defined, but in the present invention, the nitriding temperature is high, so even at 90 minutes or less, a sufficient thickness of a nitrided layer can be formed.

[0120] Note that, in the nitriding step, the gas nitriding method, nitrocarburizing method, plasma nitriding method, salt bath nitriding method, or other general nitriding method may be used.

[0121] Next, the method of production of the high strength bolt of the present invention (below, sometimes referred to as "the present invention bolts") will be explained.

[0122] The method of production of the bolt of the present invention is composed of a working step of working the steel material of the present invention having the required composition into a bolt, a decarburization step of heating the bolt to decarburize it, a hardening step of cooling the heated bolt to make the steel structure a mainly martensite structure, and a nitriding step of nitriding the hardened bolt at a temperature of over 500°C to 650°C or less.

[0123] In the nitriding step, the steel structure of the bolt becomes a mainly tempered martensite structure.

[0124] Note that, in the working step, for example, the steel material wire rod is cold forged and rolled to form a bolt.

[0125] The method of production of the bolt of the present invention differs from the method of production of the steel material of the present invention only in the working step for working the steel material into a bolt shape, so the explanation of the other steps will be omitted.

[0126] The method of production of the steel material of the present invention and the method of production of the bolt of the present invention preferably performs rapid cooling, after nitriding, in a range from 500 to 200°C by a cooling rate of 10 to 100°C/s. By rapidly cooling after nitriding, it is possible to make the compressive residual stress of the surface of the steel material or bolt 200 MPa or more. Due to the presence of this compressive residual stress, the delayed fracture resistance is improved more.

Examples

[0127] Next, examples of the present invention will be explained, but the conditions of the examples are an example of the conditions adopted for confirming the workability and effect of the present invention. The present invention is not limited to this example of the conditions. In the present invention, various conditions can be adopted so long as not departing from the gist of the present invention and achieving the object of the present invention.

(Examples)

[0128] Molten steels of the compositions of ingredients which are shown in Table 1 were cast in accordance with an ordinary method. The cast slabs were hot worked to obtain steel materials (wire rods). The steel materials were heated to A_{c3} to 950°C and cooled as is for hardening.

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[0129] Note that, at the time of heating, the atmosphere in the heating furnace was controlled to be weakly decarburizing. The hardening was performed by oil quenching so that the cooling rate in the range of 700 to 300°C became 5°C/s or more. Further, the depth of the low carbon region was investigated by the carbon potential of the atmosphere of the heating furnace, heating temperature, and holding time.

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Table 1

Steel type	Composition (mass%)																
	C	Si	Mn	Cr	V	Mo	Nb	Cu	Ni	B	Al	Ti'	Mg	Ca	Zr	Fe	V+1/2Mo
A1	0.11	2.20	1.52	0.53	0.21	0.98	0.049	3.85	2.25	0.0045	0.032	-	-	0.0003	-	Bal.	0.70
A2	0.16	2.50	1.98	0.40	-	1.21	0.039	2.01	1.01	0.0031	0.089	-	0.0003	-	0.0032	Bal.	0.61
A3	0.21	2.92	0.55	0.77	0.35	0.55	0.035	-	2.95	0.0025	-	0.012	0.0012	0.0056	0.0003	Bal.	0.63
A4	0.26	0.98	0.98	1.48	0.29	2.98	-	1.52	0.78	0.0019	0.098	0.009	0.0022	0.0031	0.0044	Bal.	1.78
A5	0.31	1.98	0.78	1.28	0.09	2.34	0.025	3.98	2.01	0.0002	-	0.031	C.0033	-	-	Bal.	1.26
A6	0.34	1.23	0.15	1.17	0.05	1.49	0.015	0.74	3.98	0.0004	0.021	0.049	0.0041	0.0021	0.0045	Bal.	0.80
A7	0.34	0.95	0.34	0.07	0.98	0.35	0.006	0.49	0.28	0.0049	0.067	0.044	-	-	-	Bal.	1.16
A8	0.41	0.61	0.45	0.64	-	1.08	0.002	-	0.01	0.0044	0.011	0.039	0.0099	0.0067	0.0036	Bal.	0.54
A9	0.41	0.35	0.72	0.29	1.48	-	0.013	0.01	-	0.0028	0.052	0.003	0.0088	0.0099	0.0079	Bal.	1.48
A10	0.45	0.20	0.12	-	1.34	0.05	0.021	0.31	0.17	0.0027	0.003	0.025	0.0052	0.0023	0.0035	Bal.	1.37
A11	0.51	0.02	0.22	0.24	0.78	0.12	0.007	0.11	0.06	-	0.033	0.021	0.0038	0.0011	0.0048	Bal.	0.84
A12	0.55	0.11	0.34	0.19	0.45	0.89	0.002	0.05	0.03	0.0034	0.026	0.033	0.0055	0.0016	0.0088	Bal.	0.90
A13	0.39	0.25	0.79	1.12	1.39	-	-	-	-	-	-	-	-	-	-	Bal.	1.39
A14	0.39	0.25	0.76	1.06	-	1.64	-	-	-	-	-	-	-	-	-	Bal.	0.82
A15	0.39	0.25	0.76	1.06	-	1.64	-	-	-	-	0.025	-	-	-	-	Bal.	0.82
B1	0.09	0.009	0.08	0.53	0.21	0.55	0.044	3.85	-	0.0045	0.032	-	-	0.0003	-	Bal.	0.49
B2	0.60	0.12	0.22	0.24	0.35	0.78	0.007	0.11	0.06	-	0.033	0.021	0.0038	0.0011	0.0048	Bal.	0.74
B3	0.34	0.95	2.10	0.12	0.21	0.69	0.006	0.49	0.28	0.0045	0.067	0.044	0.0055	0.0033	0.0068	Bal.	0.56
B4	0.21	2.54	0.55	1.60	0.15	2.03	-	-	2.95	0.0025	0.079	0.012	0.0012	0.0056	0.0011	Bal.	1.17
B5	0.31	1.98	0.78	1.28	0.25	-	0.025	0.98	2.01	0.0033	-	0.031	0.0033	0.0045	0.0012	Bal.	0.25
B6	0.31	1.98	0.78	1.28	0.09	0.75	0.025	4.1	2.01	0.0033	0.029	0.031	0.0033	-	0.0012	Bal.	0.47
B7	0.41	0.61	0.45	0.64	-	0.91	0.002	-	0.03	0.0061	0.011	0.039	0.0076	0.0067	0.0036	Bal.	0.46

"-" in the table mean deliberately not added.

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[0130] After that, the steel materials were nitrided by nitrocarburizing to form nitrided layers. After nitriding, the materials were rapidly cooled in the range of 500 to 200°C by the cooling rates which are shown in Table 2 (cooling rates after tempering) to obtain the high strength steel materials of Manufacturing Nos. 1 to 25.

5 **[0131]** Note that, the nitriding was performed at the temperatures which are shown in Table 2 while making the ammonia volume ratios in the treatment gas atmosphere 30 to 50% and making the treatment times 30 to 90 minutes.

[0132] The nitrided layers were adjusted in thickness by changing the heating temperature and the holding time. The nitrided layers were adjusted in nitrogen concentration by changing the ammonia volume ratio in the treatment gas atmosphere.

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Table 2

Man. No.	Steel type	Tempered martensite ratio (%)	Strength (MPa)	Low carbon region depth (μm)	Nitriding		Nitrided layer thickness (μm)	Compressive residual stress (MPa)	Amount of absorption of hydrogen (ppm)	Critical diffusible hydrogen content of delayed fracture (ppm)	Delayed fracture presence	Remarks
					Temperature (°C)	Cooling rate (°C/s)						
1	A1	90	1312	130	580	35	365	306	0.23	3.50	No	Inv. ex.
2	A2	87	1304	978	550	12	345	202	0.31	3.03	No	
3	A3	94	1356	556	600	53	540	405	0.45	3.13	No	
4	A4	89	1334	456	600	39	529	332	0.48	8.90	No	
5	A5	92	1427	458	600	46	511	432	0.41	6.30	No	
6	A6	98	1463	988	630	21	580	258	0.40	3.98	No	
7	A7	99	1579	954	645	43	602	384	0.39	5.78	No	
8	A8	94	1532	638	530	32	201	274	0.34	2.70	No	
9	A9	95	1502	111	600	43	509	345	0.47	7.40	No	
10	A10	98	1503	149	630	26	579	274	C.49	6.83	No	
11	A11	99	1587	105	640	78	621	456	0.42	4.20	No	
12	A12	85	1526	892	600	98	543	501	0.44	4.48	No	
13	A13	89	1478	345	620	74	601	435	0.38	4.23	No	
14	A14	91	1508	256	620	68	589	421	0.22	3.65	No	
15	A15	94	1535	339	620	65	599	411	0.23	3.33	No	

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(continued)

Man. No.	Steel type	Tempered martensite ratio (%)	Strength (MPa)	Low carbon region depth (μm)	Nitriding		Nitrided layer thickness (μm)	Compressive residual stress (MPa)	Amount of absorption of hydrogen (ppm)	Critical diffusible hydrogen content of delayed fracture (ppm)	Delayed fracture presence	Remarks
					Temperature (°C)	Cooling rate (°C/s)						
16	B1	92	1168	102	580	11	389	201	0.15	0.33	No	Comp. ex.
17	B2	93	1535	136	600	91	520	501	0.65	0.12	Yes	
18	B3	91	1546	147	620	55	550	333	0.56	0.34	Yes	
19	B4	98	1577	142	600	58	509	345	0.52	0.38	Yes	
20	B5	92	1532	165	600	45	512	312	0.63	0.41	Yes	
21	B6	94	1563	222	630	67	560	432	0.65	0.39	Yes	
22	B7	99	1564	230	600	33	530	294	0.54	0.32	Yes	
23	A3	89	1345	94	520	15	201	203	0.73	0.35	Yes	
24	A3	94	1344	205	440	18	190	204	0.63	0.26	Yes	
25	A3	92	1348	211	600	9	-	193	0.69	0.26	Yes	

(Note) Underlines in table are conditions outside scope of present invention.

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[0133] The steel materials which are shown in Table 1 (wire rods) were worked into bolts by the same process as the high strength steel materials (wire rods) of Manufacturing Nos. 1 to 25 to obtain the high strength bolts of Manufacturing Nos. 26 to 40. The nitriding was performed in the temperature ranges which are shown in Table 3. After the nitriding, the materials were rapidly cooled in the range of 500 to 200°C by the cooling rates which are shown in Table 3 (cooling rates after tempering).

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Table 3

Man. No.	Steel type	Tempered martensite ratio (%)	Strength (MPa)	Low carbon region depth (μm)	Nitriding		Nitrided layer thickness (μm)	Compressive residual stress (MPa)	Amount of absorption of hydrogen (ppm)	Critical diffusible hydrogen content of delayed fracture (ppm)	Delayed fracture presence
					Temp. (°C)	Cooling rate (°C/s)					
26	A1	90	1312	122	580	36	368	312	0.18	3.50	No
27	A2	87	1304	980	550	13	354	209	0.26	3.03	No
28	A3	94	1356	564	600	52	548	411	0.23	3.13	No
29	A4	89	1334	452	600	40	531	337	0.31	8.90	No
30	A5	92	1427	453	600	45	516	437	0.25	6.30	No
31	A6	98	1463	976	630	20	586	261	0.35	3.98	No
32	A7	99	1579	966	645	44	607	389	0.34	5.78	No
33	A8	94	1532	650	530	33	207	278	0.21	2.70	No
34	A9	95	1502	109	600	44	514	352	0.34	7.40	No
35	A10	98	1503	145	630	25	582	279	0.25	6.83	No
36	A11	99	1587	102	640	77	624	463	0.16	4.20	No
37	A12	85	1526	885	600	99	547	509	0.32	4.48	No
38	A13	89	1478	345	620	73	608	439	0.19	4.23	No
39	A14	91	1508	256	620	65	592	427	0.17	3.65	No
40	A15	94	1535	339	620	63	605	417	0.18	3.33	No

[0134] The tempered martensite ratios, tensile strengths, low carbon region depths, nitrided layer thicknesses, compressive residual stresses, amounts of absorption of hydrogen, limit amounts of diffusible hydrogen, and delayed fracture resistances of the high strength steel materials of Manufacturing Nos. 1 to 25 (Table 2) and the high strength bolts of Manufacturing Nos. 26 to 40 (Table 3) were measured by the methods which are shown below. The results are shown in Table 2 and Table 3 together.

Tempered Martensite Ratio

[0135] The tempered martensite ratio was found by polishing the cross-section of each of the high strength steel materials of Manufacturing Nos. 1 to 25 and the high strength bolts of Manufacturing Nos. 26 to 40, etching by a Nital etching solution, using an optical microscope to measure the areas of the martensite in five fields in a 0.04 mm² range, and finding the average value.

[0136] Note that in each of the high strength steel materials of Manufacturing Nos. 1 to 25 and the high strength bolts of Manufacturing Nos. 27 to 41, the structure of the remaining part of the tempered martensite was a balance of one or more of austenite, bainite, pearlite, and ferrite.

Tensile Strength

[0137] The tensile strength was measured based on JIS Z 2241.

Low Carbon Region Depth and Nitrided Layer Thickness

[0138] A cross-section of each of the high strength steel materials of Manufacturing Nos. 1 to 25 and the high strength bolts of Manufacturing Nos. 26 to 40 was polished and measured for the carbon concentration and nitrogen concentration in the depth direction from the surface using an EDX at any five locations in the longitudinal direction.

[0139] The depth (thickness) of the region where the carbon concentration is 0.9 time or less of the carbon concentration of the steel material ((carbon concentration of low carbon region/carbon concentration of steel material) ≤ 0.9) was defined as the "low carbon region depth", while the depth (thickness) of the region where the nitrogen concentration is higher than the nitrogen concentration of the steel material by 0.02% or more (nitrogen concentration of nitrided layer-nitrogen concentration of steel material ≥ 0.02) was defined as the "nitrided layer thickness".

[0140] Note that, the low carbon region depth and the nitrided layer thickness were the averages of values measured at any five locations in the longitudinal direction.

Compressive Residual Stress

[0141] An X-ray residual stress measurement apparatus was used to measure the compressive residual stress of the surface. The residual stress of the surface of each of the high strength steel materials of Manufacturing Nos. 1 to 25 and the high strength bolts of Manufacturing Nos. 26 to 40 was measured, then the surface was etched by 25 μm at a time by electrolytic polishing and the residual stress in the depth direction was measured. Note that, the compressive residual stress was made the average of the values measured at any three locations.

Critical diffusible hydrogen content and Delayed Fracture Resistance

[0142] From each of the high strength steel materials of Manufacturing Nos. 1 to 25 and the high strength bolts of Manufacturing Nos. 26 to 40, a delayed fracture test piece of the shape which is shown in FIG. 4 was prepared and subjected to absorption of hydrogen. For absorption of hydrogen, the electrolytic hydrogen charge method was used to change the charge current and change the amount of absorption of hydrogen as shown by Table 2 and Table 3.

[0143] The surface of each delayed fracture test piece which was subjected to absorption of hydrogen was plated with Cd to prevent dissipation of the diffusible hydrogen. The test piece was leaved at room temperature for 3 hours to even the concentration of hydrogen at the inside.

[0144] After that, a delayed fracture test machine which is shown in FIG. 5 was used to run a constant load delayed fracture test applying a tensile load of 90% of the tensile strength to the test piece 1. Note that, in the test machine which is shown in FIG. 5, when applying a tensile load to the test piece 1, a balance weight 2 was placed at one end of a lever having the fulcrum 3 as the fulcrum and the test piece 1 was placed at the other end to conduct the test.

[0145] Further, as shown in FIG. 1(b), the maximum value of the amount of diffusible hydrogen of a test piece 1 which did not fracture even after performing the constant load delayed fracture test for 100 hours or more was made the critical diffusible hydrogen content. The amount of diffusible hydrogen of the test piece 1 was measured by raising the delayed fracture test piece in temperature at 100°C/h and measuring the cumulative value of the amounts of hydrogen which

were released between room temperature to 400°C by a gas chromatograph.

[0146] When comparing the amount of absorption of hydrogen and the critical diffusible hydrogen content of delayed fracture and the critical diffusible hydrogen content is greater than the amount of absorption of hydrogen, delayed fracture does not occur. Conversely, if the critical diffusible hydrogen content is smaller than the amount of absorption of hydrogen, delayed fracture occurs.

[0147] Therefore, the delayed fracture resistance was evaluated as "without delayed fracture" when the amount of absorption of hydrogen which is shown in Table 2 and Table 3 was less than critical diffusible hydrogen content and as "with delayed fracture" when the amount of absorption of hydrogen was the critical diffusible hydrogen content or more.

Amount of Absorption of hydrogen

[0148] The amount of absorption of hydrogen was determined by preparing a test piece of each of the high strength steel materials of Manufacturing Nos. 1 to 25 and the high strength bolts of Manufacturing Nos. 26 to 40 and running an accelerated corrosion test of the pattern of temperature, humidity, and time which is shown in FIG. 6 for 30 cycles.

[0149] The corroded layer at the surface of the test piece was removed by sandblasting, then the hydrogen was analyzed by the Thermal desorption analysis. The amount of hydrogen which was released from room temperature to 400°C was measured to find the amount of absorption of hydrogen.

[0150] As shown in Table 2, the high strength steel materials of Manufacturing Nos. 1 to 15 of the invention examples had a low carbon region depth of 100 μm or more and a nitrided layer thickness of 200 μm or more. All had a tensile strength of 1300 MPa or more, an amount of absorption of hydrogen of 0.5 ppm or less, a critical diffusible hydrogen content of 2.00 ppm or more, an amount of absorption of hydrogen of less than the critical diffusible hydrogen content, and no delayed fracture.

[0151] Further, the high strength steel materials of Manufacturing Nos. 1 to 15 all had a tempered martensite rate of 50% or more and a structure of mainly tempered martensite. Further, the high strength steel materials of Manufacturing Nos. 1 to 15 all had a compressive residual stress of 200 MPa or more.

[0152] As opposed to this, as shown in Table 2, the high strength steel material of Manufacturing No. 16 of the comparative example was an example where the amount of C, the amount of Si, and the amount of Mn were small and the strength was low.

[0153] Manufacturing No. 17 is an example where the amount of C was large, Manufacturing No. 18 is an example where the amount of Mn was large, Manufacturing No. 19 is an example where the amount of Cr was large, Manufacturing No. 21 is an example where the amount of Cu was large, Manufacturing No. 22 is an example where the amount of B was large, and Manufacturing No. 20 is an example where V+1/2Mo was low. In each case, the critical diffusible hydrogen content was low and the resistance was "with delayed fracture".

[0154] Further, Manufacturing No. 23 is an example where the heating time of the hardening was short, the low carbon region depth was less than 100 μm, the critical diffusible hydrogen content was low, and the resistance was "with delayed fracture". Manufacturing No. 24 is an example where the nitriding time was short, the nitrided layer thickness was less than 200 μm, the amount of absorption of hydrogen was large, and the resistance was "with delayed fracture".

[0155] Manufacturing No. 25 is an example in which the concentration of ammonia in the gas of the nitriding was lowered, so at a location down to the depth of 200 μm from the surface, the difference of the nitrogen concentration from the steel material became 0.01 mass%, the amount of absorption of hydrogen was larger, and the resistance was "with delayed fracture".

[0156] As shown in Table 3, the high strength bolts of Manufacturing Nos. 26 to 40 of the invention examples had a low carbon region depth of 100 μm or more and a nitrided layer thickness of 200 μm or more. All had a tensile strength of 1300 MPa or more, an amount of absorption of hydrogen of 0.5 ppm or less, a critical diffusible hydrogen content of 2.00 ppm or more, an amount of absorption of hydrogen of less than the critical diffusible hydrogen content, and a resistance "without delayed fracture".

[0157] The high strength bolts of Manufacturing Nos. 26 to 40 all had a tempered martensite ratio of 50% or more, a structure of mainly tempered martensite, and a compressive residual stress of 200 MPa or more.

[0158] From Table 2 and Table 3, it will be understood that the high strength bolts of Manufacturing Nos. 26 to 40, which differ from the high strength steel materials of Manufacturing Nos. 1 to 15 only in the point of working the steel material (wire rod) to bolts (high strength bolts of Manufacturing Nos. 26 to 40 correspond to high strength steel materials of Manufacturing Nos. 1 to 15), were further suppressed in the amount of absorption of hydrogen compared with the high strength steel materials.

Industrial Applicability

[0159] As explained above, according to the present invention, it is possible to provide a high strength steel material (wire rod or PC steel bar) and high strength bolt which exhibit excellent delayed fracture resistance even in a severe

corrosive environment and a method of production enabling inexpensive production of these. Accordingly, the present invention is extremely high in applicability in industries manufacturing and using steel materials.

[0160] Reference Signs List

- 5 1 test piece
 2 balance weight
 3 fulcrum

10 **Claims**

1. A steel material which is excellent in delayed fracture resistance containing,

15 by mass%,
 C: 0.10 to 0.55%,
 Si: 0.01 to 3%, and
 Mn: 0.1 to 2%,

20 further containing one or both of

 V: 1.5% or less and Mo: 3.0% or less, the contents of V and Mo satisfying
 $V+1/2Mo>0.4\%$,

25 further containing one or more of

 Cr: 0.05 to 1.5%,
 Nb: 0.001 to 0.05%,
 Cu: 0.01 to 4%,
 Ni: 0.01 to 4%, and
 B: 0.0001 to 0.005%, and

30 having a balance of Fe and unavoidable impurities, the structure being a mainly tempered martensite structure, the surface of the steel material being formed with

35 (a) a nitrided layer having a thickness from the surface of said steel material of 200 μm or more and a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of said steel material by 0.02 mass% or more and

40 (b) a low carbon region having a depth from the surface of said steel material of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of said steel material.

45 2. A steel material which is excellent in delayed fracture resistance as set forth in claim 1 **characterized in that** due to the presence of said nitrided layer and low carbon region, the amount of absorption of hydrogen in the steel material is 0.5 ppm or less and the critical diffusible hydrogen content of the steel material is 2.00 ppm or more.

50 3. A steel material which is excellent in delayed fracture resistance as set forth in claim 1 or 2 further **characterized in that** said steel material contains, by mass%, one or more of

 Al: 0.003 to 0.1%,
 Ti: 0.003 to 0.05%,
 Mg: 0.0003 to 0.01%,
 Ca: 0.0003 to 0.01%, and
 Zr: 0.0003 to 0.01%.

55 4. A steel material which is excellent in delayed fracture resistance as set forth in any one of claims 1 to 3 **characterized in that** said nitrided layer has a thickness of 1000 μm or less.

5. A steel material which is excellent in delayed fracture resistance as set forth in any one of claims 1 to 4 **characterized in that** said tempered martensite has an area ratio of 85% or more.

6. A steel material which is excellent in delayed fracture resistance as set forth in any one of claims 1 to 5 **characterized in that** said steel material has a compressive residual stress at the surface of 200 MPa or more.
7. A steel material which is excellent in delayed fracture resistance as set forth in any one of claims 1 to 6 **characterized in that** said steel material has a tensile strength of 1300 MPa or more.
8. A bolt which is excellent in delayed fracture resistance obtained by working a steel material containing,
- by mass%,
 C: 0.10 to 0.55%,
 Si: 0.01 to 3%, and
 Mn: 0.1 to 2%,
- further containing one or both of
- V: 1.5% or less and
 Mo: 3.0% or less, the contents of V and Mo satisfying
 $V + 1/2Mo > 0.4\%$,
- further containing one or more of
- Cr: 0.05 to 1.5%,
 Nb: 0.001 to 0.05%,
 Cu: 0.01 to 4%,
 Ni: 0.01 to 4%, and
 B: 0.0001 to 0.005%, and
- having a balance of Fe and unavoidable impurities, the structure being a mainly tempered martensite structure, the surface of said bolt being formed with
- (a) a nitrided layer having a thickness from the surface of said bolt of 200 μm or more and a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of said steel material by 0.02 mass% or more and
- (b) a low carbon region having a depth from the surface of said bolt of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of said steel material.
9. A high strength bolt which is excellent in delayed fracture resistance as set forth in claim 8 **characterized in that** due to the presence of said nitrided layer and low carbon region, the amount of absorption of hydrogen in the bolt is 0.5 ppm or less and the critical diffusible hydrogen content of the bolt is 2.00 ppm or more.
10. A high strength bolt which is excellent in delayed fracture resistance as set forth in claim 8 or 9 **characterized in that** said steel material further contains, by mass%, one or more of
- Al: 0.003 to 0.1%,
 Ti: 0.003 to 0.05%,
 Mg: 0.0003 to 0.01%,
 Ca: 0.0003 to 0.01%, and
 Zr: 0.0003 to 0.01%.
11. A high strength bolt which is excellent in delayed fracture resistance as set forth in any one of claims 8 to 10 **characterized in that** said nitrided layer has a thickness of 1000 μm or less.
12. A high strength bolt which is excellent in delayed fracture resistance as set forth in any one of claims 8 to 11 **characterized in that** said tempered martensite has an area ratio of 85% or more.
13. A high strength bolt which is excellent in delayed fracture resistance as set forth in any one of claims 8 to 12 **characterized in that** said bolt has a compressive residual stress at the surface of 200 MPa or more.

14. A high strength bolt which is excellent in delayed fracture resistance as set forth in any one of claims 8 to 13 **characterized in that** said bolt has a tensile strength of 1300 MPa or more.

5 15. A method of production of a high strength steel material which is excellent in delayed fracture resistance as set forth in any one of claims 1 to 7,
said method of production of a high strength steel material which is excellent in delayed fracture resistance **characterized by**

10 (1) heating a steel material having a composition as set forth in claim 1 or 3 to form a low carbon region having a depth from the surface of said steel material of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of said steel material, then cooling as it is to make the steel material structure a mainly martensite structure, then

15 (2) nitriding said steel material at over 500°C to 650°C or less to form on the surface of the steel material a nitrided layer having a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of said steel material by 0.02 mass% and having a thickness from the surface of said steel material of 200 μm or more and to make the steel material structure a mainly tempered martensite structure.

20 16. A method of production of a high strength steel material which is excellent in delayed fracture resistance as set forth in claim 15 **characterized in that** said nitrided layer has a thickness of 1000 μm or less.

25 17. A method of production of a bolt which is excellent in delayed fracture resistance as set forth in any one of claims 8 to 14,
said method of production of a bolt which is excellent in delayed fracture resistance **characterized by**

30 (1) heating a bolt obtained by working a steel material having a composition as set forth in claim 8 or 10 to form a low carbon region having a depth from the surface of said bolt of 100 μm or more to 1000 μm or less and having a carbon concentration of 0.05 mass% or more and 0.9 time or less the carbon concentration of said steel material, then cooling as it is to make the steel material structure a mainly martensite structure, then

(2) nitriding said bolt at over 500°C to 650°C or less to form on the surface of the bolt a nitrided layer having a nitrogen concentration of 12.0 mass% or less and higher than the nitrogen concentration of said steel material by 0.02 mass% and having a thickness from the surface of said bolt of 200 μm or more and to make the steel material structure a mainly tempered martensite structure.

35 18. A method of production of a bolt which is excellent in delayed fracture resistance as set forth in claim 17, **characterized in that** said nitrided layer has a thickness of 1000 μm or less.

Fig.1(a)

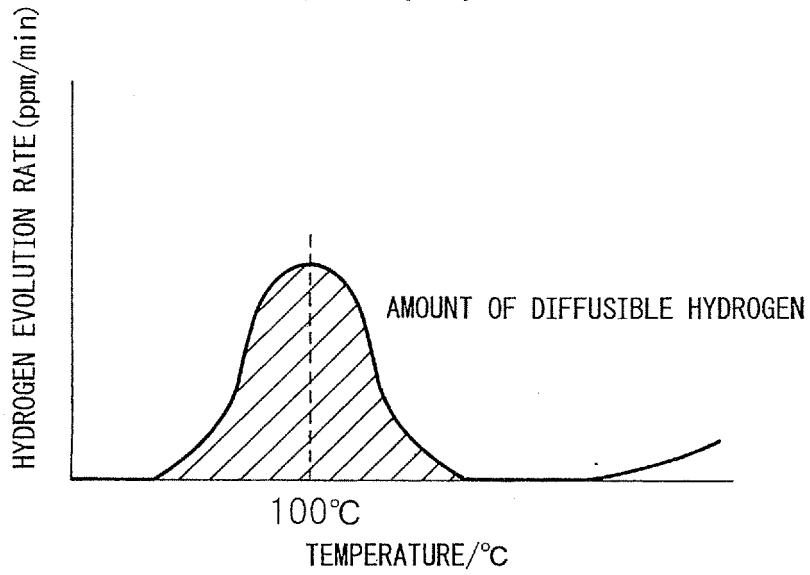


Fig.1(b)

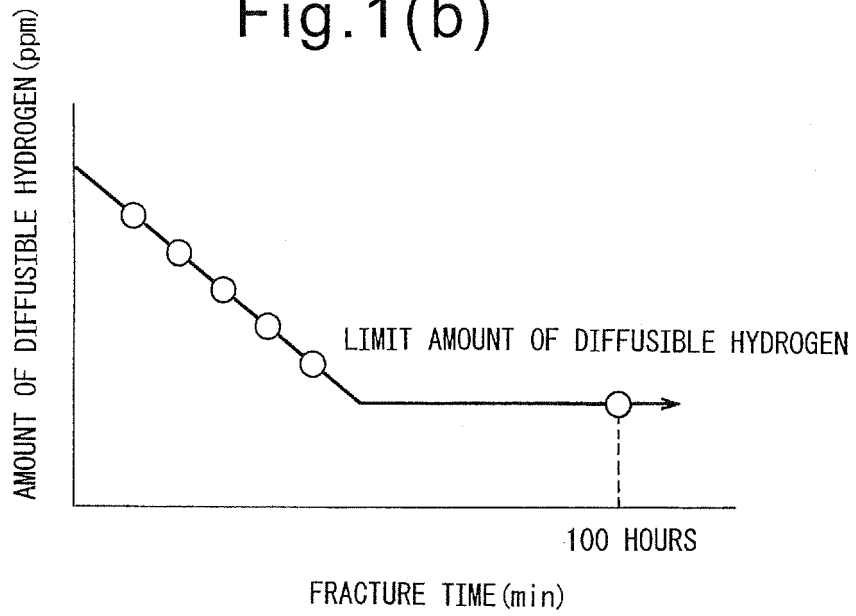


Fig.2

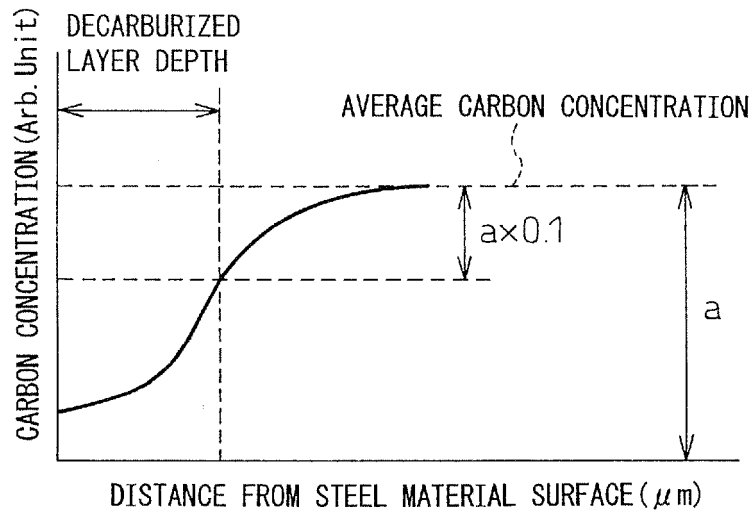


Fig.3

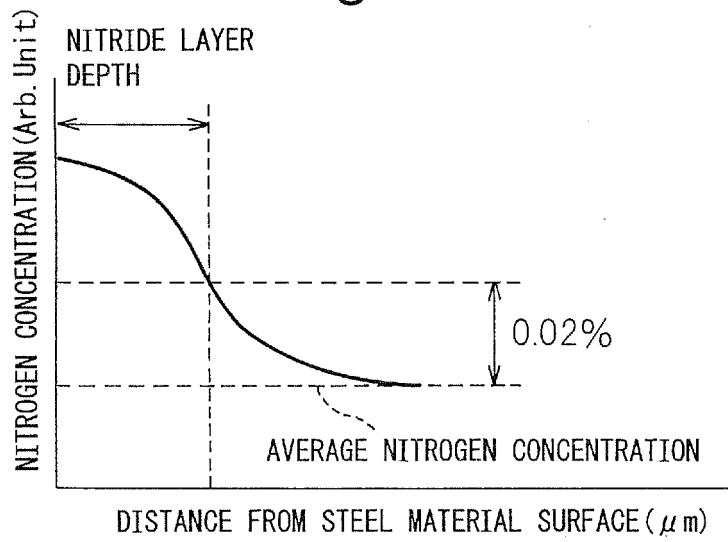


Fig.4

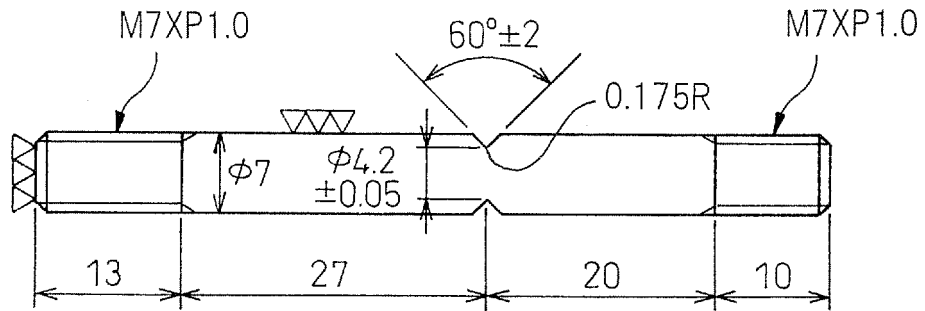


Fig.5

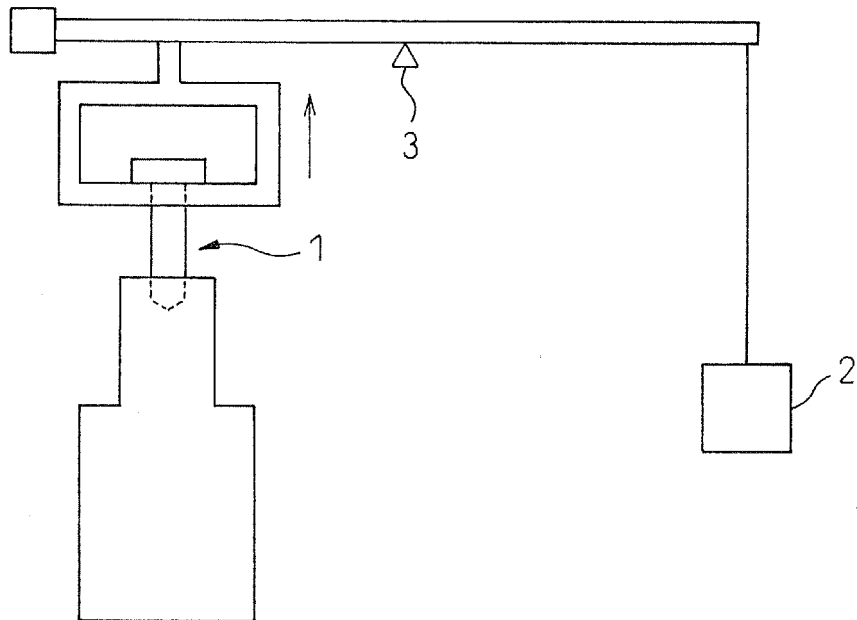
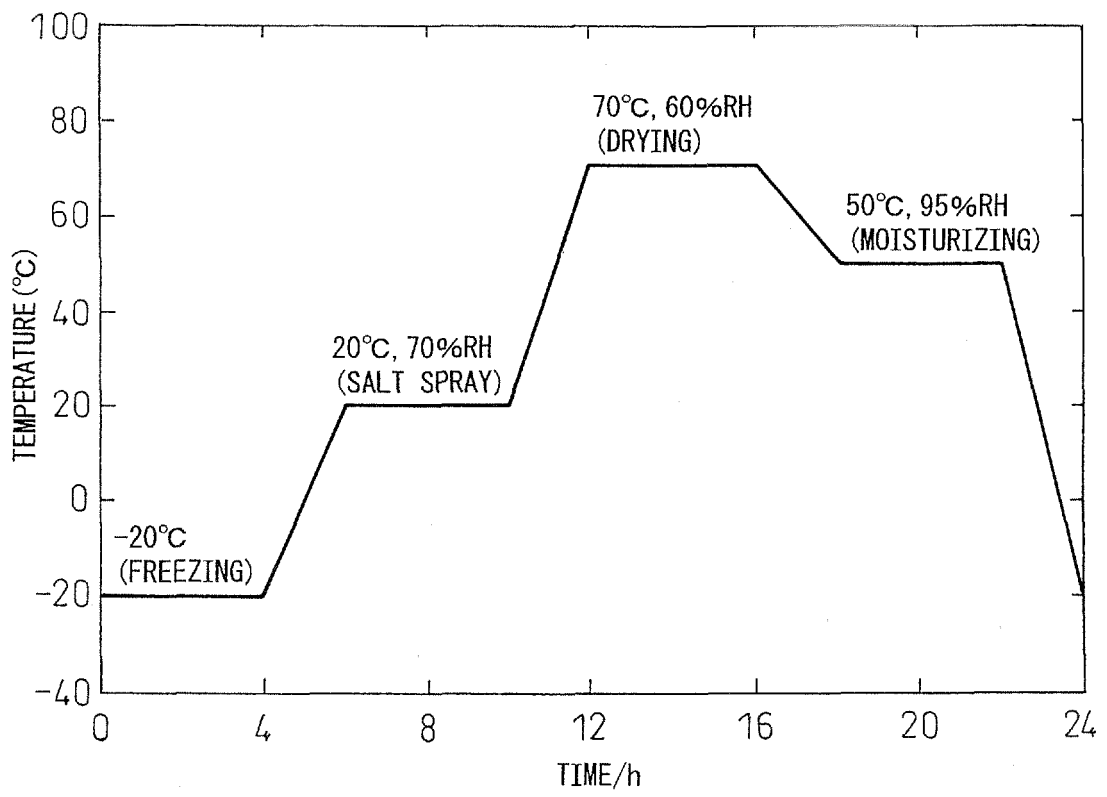


Fig.6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/056481

A. CLASSIFICATION OF SUBJECT MATTER <i>C22C38/00(2006.01)i, C21D1/06(2006.01)i, C21D1/76(2006.01)i, C21D9/00(2006.01)i, C21D9/52(2006.01)i, C22C38/58(2006.01)i, C23C8/26(2006.01)i, C23C8/30(2006.01)i</i> According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) <i>C22C38/00-38/60, C21D1/06, C21D1/76, C21D9/00, C21D9/52, C23C8/26, C23C8/30</i> Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2011 Kokai Jitsuyo Shinan Koho 1971-2011 Toroku Jitsuyo Shinan Koho 1994-2011 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-299180 A (Nippon Steel Corp.), 24 December 2009 (24.12.2009), claims (Family: none)	1-18
A	JP 10-141341 A (NKK Corp.), 26 May 1998 (26.05.1998), claims (Family: none)	1-18
A	JP 10-226817 A (Sumitomo Metal Industries, Ltd.), 25 August 1998 (25.08.1998), claims (Family: none)	1-18
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 14 June, 2011 (14.06.11)		Date of mailing of the international search report 21 June, 2011 (21.06.11)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 644566 B [0010]
- JP 3243744 A [0010]
- JP 3243745 A [0010]
- JP 2000337332 A [0010]
- JP 2000337333 A [0010]
- JP 2000337334 A [0010]
- JP 10251803 A [0010]
- JP 2009299180 A [0010]