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(54) High strength bolt having excellent hydrogen embrittlement resistance

(57) The present invention provides a high strength bolt that has excellent hydrogen embrittlement resistance.

The high strength bolt having excellent hydrogen embrittlement resistance which bolt comprises 0.20 to 0.60% of C, 1.0 to 3.0% of Si, 1.0 to 3.5% of Mn, higher than 0% and not higher than 1.5% of Al, 0.15% or less P, 0.02% or less S, and balance of iron and inevitable impurities, and the structure includes:

1% or more residual austenite;
80% or more in total content of bainitic ferrite and martensite; and
10% or less (may be 0%) in total content of ferrite and pearlite in the proportion of area to the entire structure, and also the mean axis ratio (major axis/minor axis) of the residual austenite grains is 5 or higher and the bolt has tensile strength of 1180 MPa or higher.

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Description

[0001] The present invention relates to a high strength bolt that has excellent hydrogen embrittlement resistance, particularly to a high strength bolt wherein hydrogen embrittlement, season crack and delayed fracture, that cause troubles for bolts having tensile strength of 1180 MPa or higher, are suppressed.

[0002] Low-alloy high-toughness steels, in particular SCM435 and SCM440, are widely used for manufacturing ordinary bolts. While these steels have a high tensile strength of 120 to 130 kgf/mm^2 (1180 to 1270 MPa), these steels are subjected to a refining treatment when higher strength is required.

[0003] However, refined bolts obtained through the refining treatment have the problem of delayed fracture, in which the bolt suddenly cracks upon long period of use after it was tightened in place. Japanese Patent No. 2614659 describes a method of solving this problem by adding an alloy element such as Cr, Mo, Ti and V to the basic components, and controlling the proportions of these components. Japanese Unexamined Patent Publication (Kokai) No. 2003-321743 describes that resistance against delayed fracture can be ensured by making a metal structure constituted from a single phase of tempered martensite and causing fine precipitate having a grain size smaller than 10 nm to be dispersed in the structure. With this technology, alloy element such as Ni, Ti, Mo or the like is added so as to obtain the precipitate.

[0004] However, there is a limitation to the improvement in the hydrogen storing capacity by simply controlling the form of precipitation, and it is difficult to achieve higher hydrogen embrittlement resistance by this method. Moreover, the micro alloy elements such as Ti and V are expensive and it is difficult to provide a high strength bolt that has a higher level of delayed destruction resistance at a low price. There is also such a problem that it is difficult to recycle a steel that includes much contents of the alloy elements described above.

[0005] Japanese Patent No. 3494798 describes that a bolt having tensile strength of 1300 MPa or higher and elongation of 8.8% to 12.2% can be made by controlling the structure without need for the addition of the alloy elements described above. Specifically, it is described that it suffices to form a bainite structure and control the ratio of length to width of prior austenite grains to 1.2 or higher in a region from 300 μm to 630 μm from the surface. However, further improvements are required to achieve higher hydrogen embrittlement resistance with this technology.

[0006] The present invention has been made in consideration of the problems described above, and has an object of providing a high strength bolt that has high tensile strength of 1180 MPa or higher and has significantly improved hydrogen embrittlement resistance.

[0007] The high strength bolt of the present invention comprises 0.20 to 0.60% of C (contents of components given in terms of percentage in this patent application all refer to percentage by weight), 1.0 to 3.0% of Si, 1.0 to 3.5% of Mn, higher than 0% and not higher than 1.5% of Al, 0.15% or less P, 0.02% or less S, and balance of iron and inevitable impurities, and wherein the structure includes:

1% or more residual austenite;
80% or more in total content of bainitic ferrite and martensite; and
10% or less (may be 0%) in total content of ferrite and pearlite in the proportion of area to the entire structure, wherein the mean axis ratio (major axis/minor axis) of the residual austenite grains is 5 or higher and the bolt has tensile strength of 1180 MPa or higher. This bolt shall be hereinafter referred to as the inventive bolt 1.

[0008] The high strength bolt of the present invention comprises 0.20 to 0.60% of C, 1.0 to 3.0% of Si, 1.0 to 3.5% of Mn, higher than 0% and not higher than 0.5% of Al, 0.15% or less P, 0.02% or less S, and balance of iron and inevitable impurities, and wherein the structure includes:

1% or more residual austenite;
80% or more in total content of bainitic ferrite and martensite; and
10% or less (may be 0%) in total content of ferrite and pearlite in the proportion of area to the entire structure, and wherein the mean axis ratio (major axis/minor axis) of the residual austenite grains is 5 or higher and the bolt has tensile strength of 1180 MPa or higher. This bolt shall be hereinafter referred to as the inventive bolt 2.

[0009] The high strength bolt of the present invention may also comprise higher than 0% and not higher than 0.1% of Nb and/or higher than 0% and not higher than 1.0% of Mo, or higher than 0% and not higher than 2% of Cu and/or higher than 0% and not higher than 5% of Ni.

[0010] According to the present invention, a high strength bolt having tensile strength of 1180 MPa or higher in which hydrogen infiltrating from the outside is neutralized and hydrogen embrittlement resistance is improved can be manufactured with high productivity without using expensive elements. It is also made possible to provide a high strength bolt that hardly experiences delayed fracture or such failures and is used as an automobile component at a low price. The high strength bolt of the present invention contains less alloy elements than in the prior art, and can be therefore readily recycled.

[0011] Hydrogen-induced delayed fracture is believed to occur, in tempered martensite bolt and bolt based on martensite and ferrite that have been commonly used as high strength bolts, as hydrogen is concentrated in grain boundaries of prior austenite thereby to form voids or other defects that become the start points of the fracture. Common practice that has been employed to decrease the sensitivity of delayed fracture is to diffuse fine carbide grains or the like uniformly as the trap site for hydrogen, thereby to decrease the concentration of diffusive hydrogen, as described previously as the prior art technology. However, even when a large number of carbide grains or the like are diffused uniformly as the trap site for hydrogen, there is a limitation to the hydrogen trapping capability and delayed fracture attributable to hydrogen cannot be fully suppressed.

[0012] Accordingly, the inventors of the present application studied the means of achieving higher hydrogen embrittlement resistance (delayed fracture resistance) while fully taking into account the environment where the bolt is used.

[0013] The inventors reached such a conclusion that the best way of improving the hydrogen embrittlement resistance by decreasing the number of intergranular fracture initiating points is to form the matrix phase of the bolt from a binary structure of bainitic ferrite and martensite with the bainitic ferrite acting as the main phase, not the single phase structure of martensite that is generally used for high strength bolts. In the single phase structure of martensite, a carbide (for example, film-like cementite) is likely to precipitate in the grain boundaries, thus making intergranular fracture likely to occur. In the case of the binary structure of bainitic ferrite and martensite with the bainitic ferrite acting as the main phase, in contrast, the bainitic ferrite takes the form of plate-like ferrite that has higher dislocation density, unlike the ordinary (polygonal) ferrite, and allows it to easily increase the strength of the entire structure as in the case of the single phase of martensite while improving the hydrogen embrittlement resistance as much hydrogen is trapped in the dislocations. It also has such an advantage that coexistence of the bainitic ferrite and residual austenite which will be described later prevents the generation of carbide that acts as the intergranular fracture initiating points.

[0014] It was also found that it is very effective to form lath-shaped residual austenite for increasing the hydrogen trapping capacity and neutralizing hydrogen, thereby to improve hydrogen embrittlement resistance. It has been believed in the past that residual austenite has an adverse effect on hydrogen embrittlement resistance and fatigue characteristic. However, according to the research conducted by the present inventors, it was found that the residual austenite has a form of blocks on the order of micrometers which adversely affects the hydrogen embrittlement resistance and fatigue characteristic, though controlling the form of residual austenite in lath shape of size on the order of sub-micrometers makes it possible to put the hydrogen storing capability of the residual austenite into full play so as to store and trap much hydrogen thereby to achieve significant improvement of hydrogen embrittlement resistance.

[0015] The reason for specifying the structures of the bolt of the present invention will now be described in detail below.

[0016] <Bainitic ferrite (BF) and martensite (M): 80% or more >

The bolt of the present invention is made in binary phase structure of bainitic ferrite and martensite (bainitic ferrite is the main phase). As described previously, bainitic ferrite is a hard structure and enables it to achieve high strength of the bolt. Also because the matrix phase has high density of dislocations so that much hydrogen can be trapped in the dislocations, higher hydrogen storing capability than other types of TRIP bolt is obtained. Moreover there is such an advantage that the lath-shaped residual austenite specified in the present invention is readily generated in the boundary between the lath-shaped bainitic ferrite grains, thereby giving the bolt excellent drawability. In order to achieve these effects efficiently, total area of bainitic ferrite and martensite is set to 80% or more, preferably 85% or more and more preferably 90% or more in proportion to the entire structure. Upper limit of the proportion may be determined by the balance with other structure (residual austenite), and is set to 99% when other structure (ferrite, etc.) than the residual austenite is not contained.

[0017] The bainitic ferrite is a lower structure having high density of dislocations consisting of plate-shaped ferrite. It is clearly distinguished from polygonal ferrite that has a lower structure containing no or very low density of dislocations, by SEM observation as follows.

[0018] Area proportion of bainitic ferrite structure is determined as follows. A test piece (columned shape) is cut off so that a position one half of the diameter in the cross section can be observed, and the surface is etched with Nital etchant. A measurement area (about 50 by 50 μm) at an arbitrarily chosen position in the surface is observed with a magnification factor of 1500 by means of a scanning electron microscope (SEM).

[0019] Bainitic ferrite is shown with dark gray color in SEM photograph (bainitic ferrite, residual austenite and martensite may not be distinguishable in the case of SEM observation), while polygonal ferrite is shown black in SEM photograph and has polygonal shape that does not contain residual austenite and martensite inside thereof.

[0020] The SEM used in the present invention is a high-resolution FE-SEM (Field Emission type Scanning Electron Microscope XL30S-FEG manufactured by Philips Inc.) equipped with an EBSP (Electron Back Scattering Pattern) detector, that has a merit of being capable of analyzing the area observed by the SEM at the same time with the EBSP detector. EBSP detection is carried out as follows. When the sample surface is irradiated with electron beam, the EBSP detector analyzes the Kikuchi pattern obtained from the reflected electrons, thereby to determine the crystal orientation at the point where the electron beam has hit upon. Distribution of orientations over the sample surface can be measured by scanning the electron beam two-dimensionally over the sample surface while measuring the crystal orientation at

predetermined intervals. The EBSP detection method has such an advantage that different structures that are regarded as the same structure in the ordinary microscopic observation but have different crystal orientations can be distinguished by the color tone.

[0021] <Residual austenite (residual γ, γ_R): 1% or more >

Residual austenite, that contributes not only to the improvement of total elongation as has been known in the prior art but also to the improvement of hydrogen embrittlement resistance, is contained in a proportion of 1% or more in the bolt of the present invention. The proportion is preferably 2% or more, and more preferably 3% or more. Excessive content of the residual austenite makes it unable to achieve a desired strength, and therefore it is recommended to set an upper limit of 20% to the proportion. The upper limit is more preferably 15%.

[0022] The inventors found that, when the residual austenite has lath shape, hydrogen trapping capability far exceeding that of carbide is obtained and, in case the shape has mean axis ratio (major axis/minor axis) of 5 or higher, hydrogen that infiltrates through the so-called atmospheric corrosion can be substantially neutralized thereby greatly improving the hydrogen embrittlement resistance, as described previously. Mean axis ratio of the residual austenite is preferably 10 or higher, more preferably 15 or higher.

[0023] In view of stability of the residual austenite, it is recommended to control the C concentration ($C_{\gamma R}$) in the residual austenite to 0.8% or higher. When the value of $C_{\gamma R}$ is controlled to 0.8% or higher, it is also made possible to improve the elongation characteristic and other properties effectively. $C_{\gamma R}$ is preferably 1.0 or higher and more preferably 1.2% or higher. While it is preferable that C_{YR} is as high as possible, it is considered that in practice there is an upper limit of around 1.6%.

[0024] The residual austenite refers to a region that is observed as FCC (face centered cubic lattice) by the FE-SEM/EBSP method. Measurement by the EBSP may be done, for example, by measuring a measurement area (about 50 by 50 μm) at an arbitrarily chosen position in the cross section of a test piece (columned shape) at a position of one half of the diameter at measuring intervals of 0.1 μm, as in the case of the observation of the bainitic ferrite and martensite. The measuring surface is prepared by electrolytic polishing in order to prevent the residual austenite from transforming. Then the test piece is set in the lens barrel of the FE-SEM equipped with the EBSP detector and is irradiated with electron beam. An EBSP image projected onto a screen is captured by a high sensitivity camera (VE-1000-SIT manufactured by Dage-MTI Inc.) and is sent to a computer. The computer carries out image analysis and generates color mapping of the FCC phase through comparison with a structural pattern simulated with a known crystal system (FCC (face centered cubic lattice) phase in the case of residual austenite). Area proportion of the region that is mapped as described above is taken as the area proportion of the residual austenite. This analysis was carried out by means of hardware and software of OIM (Orientation Imaging Microscopy™) system of TexSEM Laboratories Inc.

[0025] The mean axis ratio was determined by measuring the major axis and minor axis of residual austenite crystal grain existing in each of three arbitrarily chosen fields of view in the observation by means of TEM (transmission electron microscope) with magnification factor of 15000, and averaging the ratios of major axis to minor axis.

[0026] <Ferrite (F) + pearlite (P): 10% or less (may be 0%) >

The bolt of the present invention may be constituted from only the structure described above (mixed structure of bainitic ferrite + martensite and residual austenite). However, other structures of ferrite (which refers to polygonal ferrite, namely ferrite that contains no or very low density of dislocations) and/or pearlite to such an extent that does not compromise the effects of the present invention. While these structures may inevitably remain in the bolt through the manufacturing process of the present invention, their content is preferably as small as possible and is controlled to not higher than 10%, preferably below 5% and more preferably below 3%, according to the present invention.

[0027] The present invention is characterized in that the metallurgical structure is controlled as described above. In order to form such a structure and improve the hydrogen embrittlement resistance and increase the strength, it is necessary to control the composition of the bolt as follows.

[0028] <C: from 0.20 to 0.60%>

C is an essential element required to ensure high strength of 1180 MPa or higher and retain the residual austenite. Particularly it is important to contain a sufficient content of C in the austenite phase, so as to maintain the desired austenite phase to remain at the room temperature. In order to make use of this action, it is necessary to contain 0.20% or more C content, preferably 0.25% or more. Since excessive C content decreases the toughness and therefore leads to lower hydrogen embrittlement resistance, C content is controlled within 0.60%, preferably 0.5% or lower.

[0029] <Si: 1.0 to 3.0%>

Si is an important element that effectively suppresses the residual austenite from decomposing and carbide from being generated, and is also a substitution type solid solution strengthening element that is effective for hardening the material. In order to make full use of these effects, it is necessary to contain Si in a concentration of 1.0% or higher, preferably 1.2% or higher and more preferably 1.5% or higher. However, excessively large content of Si decreases the toughness and leads to lower hydrogen embrittlement resistance, Si content is controlled within 3.0%, preferably within 2.7% and more preferably within 2.5%.

[0030] <Mn: 1.0 to 3.5%>

Mn is an element required to stabilize austenite phase and obtain the desired level of residual austenite. In order to make full use of this effect, it is necessary to contain Mn in a concentration of 1.0% or higher, and preferably 1.2% or higher and more preferably 1.5% or higher. However, since excessive content of Mn leads to conspicuous segregation and results in poor machinability, Mn content is controlled within 3.5%, preferably within 3.2% and more preferably within 3.0%.

[0031]

<Al: 1.5% or less (higher than 0%)> (In the case of inventive bolt 1)
<A1: 0.5% or less (higher than 0%)> (In the case of inventive bolt 2)

0.01% or higher content of Al may be contained for the purpose of deoxidation. In addition to deoxidation, Al also has the effects of improving the corrosion resistance and improving hydrogen embrittlement resistance.

[0032] The mechanism of improving the corrosion resistance is supposedly based on the improvement of corrosion resistance of the matrix per se and the effect of formation rust generated by atmospheric corrosion, while the effect of formation rust presumably has greater contribution. This is supposedly because the formation rust is denser and better in protective capability than ordinary iron rust, and therefore checks the progress of atmospheric corrosion so as to decrease the amount of hydrogen generated by the atmospheric corrosion, thereby to effectively suppress the occurrence of hydrogen embrittlement, and hence the delayed fracture.

[0033] While details of the mechanism of improvement of the hydrogen embrittlement resistance by Al is not known, it is supposed that condensing of Al on the surface of the bolt makes it difficult for hydrogen to infiltrate into the bolt, and the decreasing diffusion rate of hydrogen in the bolt makes it difficult for hydrogen to migrate so that hydrogen embrittlement becomes less likely to occur. In addition, stability of lath-shaped residual austenite improved by the addition of Al is believed to contribute to the improvement of hydrogen embrittlement resistance.

[0034] In order to effectively achieve the effects of Al in improving the corrosion resistance and improving the hydrogen embrittlement resistance, Al content is controlled to 0.02% or higher, preferably 0.2% or higher and more preferably 0.5% or higher.

[0035] However, Al content must be controlled within 1.5% in order to keep inclusions such as alumina from increasing in number and size so as to ensure satisfactory machinability, ensure the generation of fine residual austenite, suppress corrosion from proceeding with the inclusion containing Al as the starting point, and prevent the manufacturing cost from increasing. In view of the manufacturing process, it is preferable to control so that A_3 point is not higher than 1000°C.

[0036] As the Al content increases, inclusions such as alumina increase and delayed fracture resistance becomes poorer. In order to suppress the generation of the inclusions such as alumina and make a bolt having higher delayed fracture resistance, Al content is restricted within 0.5%, preferably within 0.3% and more preferably within 0.1%.

[0037] <P: 0.15% or lower)

P is an element that promotes intergranular fracture due to intergranular segregation. Therefore, P content is preferably as low as possible with an upper limit set to 0.15%. P content is controlled to preferably within 0.1%, and more preferably within 0.05%.

[0038] <S: 0.02% or lower>

S is an element that promotes absorption of hydrogen in the bolt in corrosive environment. S content is controlled to within 0.02%, and preferably within 0.01%.

[0039] While composition of the bolt of the present invention is as described above with the rest substantially consisting of Fe, it may contain inevitable impurities introduced into the bolt depending on the stock material, production material, manufacturing facility and other circumstances, containing 0.01% or less nitrogen. In addition, other elements as described below may be intentionally added to such an extent that does not adversely affect the effects of the present invention.

[0040] <Nb: 0.1% or lower (higher than 0%) and/or Mo: 1.0% or lower (higher than 0%)

Nb has great effect in increasing the strength of the bolt and decreasing the grain size, and the effects can be enhanced by adding Nb and Mo together. It is recommended to add 0.005% or more (preferably 0.01% or more) Nb in order to achieve the effects described above. However, the effects described above reach saturation when excessive Nb content is contained, resulting in economical disadvantage. Therefore, Nb content is limited to 0.1% or less.

[0041] Mo has the effects of stabilizing austenite so as to retain residual austenite, impeding the infiltration of hydrogen so as to improve hydrogen embrittlement resistance and improving the hardenability of the bolt. It also has the effect of strengthening the grain boundary so as to suppress hydrogen embrittlement from occurring. It is recommended to add 0.005% or more (preferably 0.01% or more) Mo in order to achieve these effects. However, since the effects described above reach saturation when excessive Mo content is contained, resulting in economical disadvantage, Mo content is limited to 1.0% or less.

[0042] <Cu: 2% or lower (higher than 0%) and/or Ni: 5% or lower (higher than 0%)

Addition of Cu and/or Ni enables it to effectively suppress the generation of hydrogen that causes hydrogen embrittlement,

and at the same time suppress hydrogen that has been generated from infiltrating into the bolt. As a result, diffusive hydrogen concentration in the bolt can be decreased to a harmless level by the synergy effect of the effects of these elements and the effects of the composition described above to improve the hydrogen trapping capability of the bolt.

[0043] Specifically, Cu and Ni have the effect of improving the corrosion resistance of the bolt itself thereby to suppress the generation of hydrogen through corrosion of the bolt. These elements also have the effect of promoting the generation of iron oxide, a-FeOOH, that is believed to be particularly stable thermodynamically and have protective property among various forms of rust generated in the atmosphere. By assisting the generation of this rust, it is made possible to suppress hydrogen that has been generated from infiltrating into the bolt thereby to sufficiently improve the hydrogen embrittlement resistance to endure in harsh corrosive environment. This effect can be achieved particularly satisfactorily when Cu and Ni are contained at the same time.

[0044] In order to achieve the effects described above, concentration of Cu, if added, is preferably 0.03% or higher and more preferably 0.1% or higher, and concentration of Ni, if added, is preferably 0.03% or higher and more preferably 0.1% or higher.

[0045] Since excessively high concentration of either Cu or Ni is detrimental to machinability, it is preferable to limit the Cu content to 2% or lower (more preferably 1.5% or lower) and limit the Ni content to 5% or lower (more preferably 3% or lower).

[0046] <Cr: 2% or lower (higher than 0%)>

Cr is a useful element that improves hardenability without hardly affecting the deformability, thereby to easily achieve high strength. In order to fully achieve this effect, it is preferable that 0.1% or more Cr is contained. However, excessively high concentration of Cr leads to the generation of cementite that makes it difficult for residual austenite to remain, and therefore concentration of Cr is preferably controlled within 2%.

[0047] <Ti and/or V: 0.003 to 1.0% in total>

Ti has the effect of assisting in the generation of protective rust, similarly to Cu and Ni. The protective rust has a very valuable effect of suppressing the generation of β-FeOOH that appears in chloride environment and has adverse effect on the corrosion resistance (and hence on the hydrogen embrittlement resistance). Formation of such a protective rust is promoted particularly by adding Ti and V (or Zr). Ti renders the bolt excellent corrosion resistance, and also has the effect of cleaning the bolt.

[0048] V is effective in increasing the strength of the bolt and decreasing the crystal grains, in addition to having the effect of improving hydrogen embrittlement resistance through cooperation with Ti, as described previously.

[0049] In order to fully achieve the effect of Ti and/or V described above, it is preferable to add Ti and/or V to total concentration of 0.003% or higher (more preferably 0.01% or higher). For the purpose of improving hydrogen embrittlement resistance, in particular, it is preferable to add more than 0.03% of Ti, more preferably 0.05% or more Ti. However, the effects described above reach saturation when an excessive amount of Ti is added, resulting in economical disadvantage. Excessive V content also increases the precipitation of much carbonitride and leads to poor machinability and lower hydrogen embrittlement resistance. Therefore, it is preferable to control the total concentration of Ti and/or V to within 1.0%, more preferably within 0.8%.

[0050] <Zr: 0.003 to 1.0%>

Zr is effective in increasing the strength of the bolt and decreasing the crystal grain size, and also has the effect of improving hydrogen embrittlement resistance through cooperation with Ti. In order to sufficiently achieve these effects, it is preferable that 0.003% or more Zr is contained. However, excessive Zr content increases the precipitation of carbonitride and leads to poor machinability and lower hydrogen embrittlement resistance. Therefore, it is preferable to control the concentration of Zr to within 1.0%.

[0051] <B: 0.0002 to 0.01%>

B is effective in increasing the strength of the bolt, and it is preferable that 0.0002% or more (more preferably 0.0005% or more) B is contained. However, excessive content of B leads to poor hot machinability. Therefore, it is preferable to control the concentration of B to within 0.01% (more preferably within 0.005%).

[0052] The present invention does not specify the manufacturing conditions, but asserts it that stud bolts or the like can be manufactured by forging a steel that has the composition specified in the present invention and forming threads by thread rolling on both end portions, or forming a bolt head at one end by warm forging and forming threads by thread rolling on both end portions, or forming a bolt head at one end by warm forging or turning operation. In this case, in order to form the structure described above that can improve the hydrogen embrittlement resistance and strength at the same time, it is recommended to carry out the rolling operation at a finishing temperature of A_3 point or higher. When the finishing temperature is lower than A_3 point, C does not diffuse sufficiently and the desired bainitic ferrite structure and residual austenite structure cannot be obtained.

[0053] When the finishing temperature is too high, austenite grains grow and it becomes impossible to form fine residual austenite structure. Therefore, the finishing temperature is preferably set to (A_3 point +100°C) or lower, and more preferably (A_3 point +50°C) or lower.

[0054] Then the material is cooled down. According to the present invention, it is recommended to cool down the wire

at a mean cooling rate of 3°C/s or higher to a temperature in a range from (M_s point -50°C) to B_s point and keep the material at this temperature for a period of 60 to 3600 seconds.

[0055] The reason for cooling down the material at the mean cooling rate of 3°C/s or higher is to form the desired bainitic ferrite structure and avoid the formation of pearlite structure that is undesirable for the present invention. The mean cooling rate is preferably as high as possible, and it is recommended to set it to 10°C/s or higher (more preferably 20°C/s or higher).

[0056] Then the material is quenched to a temperature between (M_s point -50°C) and Bs point, followed by isothermal transformation, thereby to form the desired structure. When the heat retaining temperature becomes higher than Bs point, pealite structure that is undesirable for the present invention is formed, thus making it impossible to obtain the desired bainitic ferrite structure. When the heat retaining temperature is lower than (M_s point -50°C), area proportion of residual austenite becomes smaller.

[0057] When the heat retaining period is longer than 3600 seconds, residual austenite decomposes and cementite is formed, leading to failure to achieve the desired performance. When the heat retaining period is shorter than 60 seconds, sufficient diffusion of C does not occur and residual austenite cannot be formed, in which case again leading to failure to achieve the desired performance. The heat retaining period is preferably in a range from 100 to 3000 seconds, more preferably from 180 to 2400 seconds.

[0058] The high strength bolt of the present invention may be high-tension bolt, torque shear-type bolt, galvanized high strength bolt, rust-proof high strength bolt and flame resistant high strength bolt, and can be used as bolts having high strength and high hydrogen embrittlement resistance suitable for automobile, architecture, industrial machinery and other fields.

[0059] The present invention will now be described below by way of examples, but the present invention is not limited to the example. Various modifications may be conceived without departing from the spirit of the present invention.

[0060] Sample steels A through Q having the compositions shown in Table 1 were heated, to (A_3 point +30°C) for Nos. 1 through 14 and 16 through 21 and 780°C for No. 15, for a period of 60 to 1800 seconds, quenched to the temperature of To shown in Table 2 and were held at the temperature (To) for t seconds as shown in Table 2, and was left to cool down. While the samples were made in this procedure in the Example, such a procedure may also be employed as the material is rolled at (A_3 point +30°C), cooled down to the room temperature, then heated again to (A_3 point +30°C), held at this temperature for 60 to 1800 seconds, quenched to the temperature of To shown in Table 2 and held at the temperature (To) for t seconds as shown in Table 2, and is left to cool down.

[0061] The samples obtained as described above were investigated for the metal structure, tensile strength (TS), elongation (total elongation E1), hydrogen embrittlement resistance and fatigue characteristic in the following procedure.

[0062] Observation of metal structure

The test pieces (10mm in diameter) prepared as described above were observed and photographed in a measurement area (about 50 by 50 μm at measuring intervals of 0.1 μm) at an arbitrarily chosen position in the cross section of the test piece at a position of one half of the diameter, and area proportion of bainitic ferrite (BF) and martensite (M) and area proportion of residual austenite (residual γ) were measured by the method described previously. Similar measurements were made in two fields of view that were arbitrarily selected, and the measured values were averaged. Proportions of other structures were determined by subtracting the area proportions of these structures. Mean axis ratio of the residual austenite crystal grains was determined by the method described previously.

[0063] Measurement of tensile strength

The various types of bolts were machined to make tensile strength test pieces measuring 8 mm in diameter. These test pieces were subjected to tensile strength test to measure the tensile strength (TS).

[0064] Evaluation of hydrogen embrittlement resistance

Samples having tensile strength of 1180 MPa or higher were subjected to the evaluation of hydrogen embrittlement resistance. The various specimens were machined to make delayed fracture test pieces with annular notch (measuring 8 mm in diameter in parallel portion and 6 mm in diameter in notched portion). The test pieces were subjected to hydrogen charge with current density of 1.0 mA/cm^2 in dilute sulfuric acid of pH 3.0 (liquid temperature 30°C), and were subjected to loading with the load varied at 10% steps in a range from 30% to 80% of the ST, and the time before rupture was measured. Then the load stress with rupture time of 200 hours was determined from the relationship between the load and the rupture time. Crack fracture strength ratio was defined as the load stress with rupture time of 200 hours of hydrogen-charged test piece divided by the load stress with rupture time of 200 hours of test piece not subjected to hydrogen charge, and the crack fracture strength ratio was used as an index of hydrogen embrittlement resistance. In consideration of the fact that SCM435 that is widely used to manufacture bolts having tensile strength of 1000 MPa class has delayed fracture strength ratio of about 0.5 at the most, samples having delayed fracture strength ratio of 0.5 or higher were evaluated to have high hydrogen embrittlement resistance.

[0065] Some kinds of bolt were subjected to hydrogen charge four-point bending test. In this test, rectangular test pieces measuring 65 mm by 8 mm made of the various types of bolts described above were immersed in (0.5 mol/H_2SO_4 + 0.01 mol/KSCN) solution and were cathodically charged with hydrogen, so as to measure the maximum stress that

was endured for 1 hour without rupture as the critical fracture load (DFL). Ratio of this value to the value of DFL of experiment No. 1 (bolt A) shown in Table 2 was determined.

[0066] The test results are shown in Table 2.

[0067]

Table 1

Type of steel	Formulation of chemical components* (mass%)												Ac3 (°C)	Bs (°C)	Ms (°C)
	C	Si	Mn	Al	P	S	Nb	Mo	Cu	Ni	Ti	Others			
A	0.41	2.03	2.97	0.033	0.03	0.003	-	-	-	-	-	-	815.9	452.0	268.7
B	0.38	2.01	2.52	0.031	0.03	0.003	0.05	-	-	-	-	-	832.5	500.6	297.7
C	0.40	1.98	2.30	0.033	0.03	0.002	-	0.3	-	-	-	-	844.8	490.1	289.2
D	0.40	2.00	2.03	0.032	0.02	0.003	-	-	0.3	-	-	-	830.9	539.3	304.4
E	0.41	1.97	2.00	0.033	0.02	0.003	-	-	-	0.3	-	-	830.7	528.2	295.6
F	0.35	1.48	2.49	0.032	0.02	0.002	-	-	-	-	0.05	-	828.2	511.4	312.9
G	0.29	1.98	1.99	0.033	0.03	0.003	-	-	-	-	0.08	-	895.7	572.6	357.9
H	0.51	2.01	2.47	0.032	0.02	0.003	-	-	-	-	-	Cr:0.05	807.6	470.0	237.8
I	0.15	2.52	3.02	0.031	0.02	0.003	0.05	-	-	-	-	-	879.8	517.7	390.2
J	0.41	0.49	2.48	0.033	0.02	0.002	-	0.5	-	-	-	-	770.5	454.6	274.3
K	0.70	2.01	2.01	0.033	0.013	0.003	-	-	-	-	-	-	792.0	460.1	162.9
L	0.41	2.02	2.48	0.051	0.03	0.003	-	-	-	-	-	-	837.3	496.1	284.8
M	0.40	1.98	2.50	0.321	0.03	0.002	0.05	-	-	-	-	-	944.5	497.0	288.9
N	0.42	2.00	2.51	0.422	0.03	0.002	-	0.3	-	-	-	-	991.8	465.8	272.8
O	0.41	1.97	2.51	0.541	0.03	0.002	0.05	0.2	-	-	-	-	1036.5	476.8	279.6
P	0.42	1.98	2.55	0.72	0.03	0.002	0.05	0.2	-	-	-	-	1105.7	470.5	273.6
Q	0.40	2.01	2.60	1.60	0.03	0.002	0.05	0.2	-	-	-	-	1460.8	471.4	281.4

*: balance of iron and inevitable impurities

[0068]

Table 2

Test No.	Type of steel	To	t	Residual γ	Mean axis ratio of residual austenite crystal grains	BF + M	F	TS	Strength ratio of delayed fracture	DFL ratio
		(°C)	Sec	Area %	-	Area %	Area %	MPa	-	
1	A	300	1800	13	o	87	0	1490	0.67	1.00
2	B	300	1800	12	o	88	0	1510	0.65	-
3	C	300	1800	11	o	89	0	1560	0.63	-
4	D	320	1800	11	o	89	0	1530	0.65	-
5	E	320	1800	12	o	88	0	1520	0.67	-
6	F	320	1200	9	o	91	0	1620	0.65	-
7	G	320	600	8	o	92	0	1650	0.61	-
8	H	300	2400	14	o	86	0	1710	0.59	-
9	I	350	1200	5	o	92	3	1090	-	-
10	J	320	1200	1	×	99	0	1330	0.44	-
11	K	350	1200	15	o	85	0	1490	0.41	-
12	A	550	1800	0*	×	0*	40*	760	-	-
13	A	350	7200	1	×	99	0	1380	0.42	-
14	A	320	10	1	×	99	0	1820	0.27	-
15	A	400	600	2	×	68	30	1540	0.38	-
16	L	320	1800	13	o	87	0	1494	0.68	1.19
17	M	320	1800	13	o	87	0	1497	0.69	1.49
18	N	320	1800	14	o	86	0	1499	0.70	1.58
19	O	320	1800	14	o	86	0	1501	0.72	1.58
20	P	320	1800	14	o	86	0	1513	0.73	1.63
21	Q	320	1800	15	×	55	30	1211	0.35	0.79

*: balance of Pearlite

[0069] The test results shown in Tables 1 and 2 can be interpreted as follows (numbers in the following description refer to the experiment Nos. given in Table 2).

[0070] Nos. 1 through 8 and 16 through 20 that satisfy the requirements of the present invention show high strength of 1180 MPa or higher and high hydrogen embrittlement resistance to endure harsh corrosive environment. Nos. 16 through 20 show particularly excellent hydrogen embrittlement resistance.

[0071] Nos. 9 through 15 and 21 that do not satisfy the requirements of the present invention have the following drawbacks.

[0072] No. 9 does not have the strength specified in the present invention due to insufficient C content.

[0073] No. 10 has poor hydrogen embrittlement resistance because it dose not have a desired residual γ due to insufficient Si content.

[0074] No. 11, that was made from bolt K having excessive C content, showed poor hydrogen embrittlement resistance and poor fatigue characteristic due to precipitation of carbide.

[0075] Nos. 12 through 15 were made of steels having the composition specified in the present invention, but had some defects because they were not manufactured under the recommended conditions.

[0076] No. 12 failed to show a high strength, because it was subjected to austempering treatment at an excessively high temperature, and therefore bainitic ferrite, martensite and residual γ could not be retained.

[0077] No. 13 was subjected to austempering treatment for an excessively long period of time, No. 14 was subjected to austempering treatment for too short a period of time and No. 15 was subjected to heating in a two-phase region (780 °C), and therefore all of these samples developed polygonal form of residual γ, resulting in poor hydrogen embrittlement resistance.

[0078] No. 21 contained Al content higher than that specified for the inventive bolt 1, and therefore retained the predetermined amount of residual austenite, but the residual austenite did not satisfy the requirement for the mean axis ratio specified in the present invention, did not form the desired matrix phase while inclusions such as AlN were formed, thus resulting in poor hydrogen embrittlement resistance.

Claims

1. A high strength bolt having excellent hydrogen embrittlement resistance, which comprises:

0.20 to 0.60% of C,
1.0 to 3.0% of Si,
1.0 to 3.5% of Mn,
higher than 0% and not higher than 1.5% of Al,
0.15% or less P,
0.02% or less S,
and balance of iron and inevitable impurities,

wherein the structure includes:

1% or more of residual austenite;
80% or more in total content of bainitic ferrite and martensite; and
10% or less (may be 0%) in total content of ferrite and pearlite in the proportion of area to the entire structure, and wherein the mean axis ratio (major axis/minor axis) of the residual austenite grains is 5 or higher and the steel has tensile strength of 1180 MPa or higher.

2. A high strength bolt having excellent hydrogen embrittlement resistance, which comprises:

0.20 to 0.60% of C,
1.0 to 3.0% of Si,
1.0 to 3.5% of Mn,
higher than 0% and not higher than 0.5% of Al,
0.15% or less P,
0.02% or less S,
and balance of iron and inevitable impurities,

wherein the structure includes:

1% or more residual austenite;
80% or more in total content of bainitic ferrite and martensite; and
10% or less (may be 0%) in total content of ferrite and pearlite in the proportion of area to the entire structure, and wherein the mean axis ratio (major axis/minor axis) of the residual austenite grains is 5 or higher and the steel has tensile strength of 1180 MPa or higher.

3. A high strength bolt having excellent hydrogen embrittlement resistance according to the claim 1 or 2, which further comprises:

higher than 0% and not higher than 0.1% of Nb and/or higher than 0% and not higher than 1.0% of Mo.

4. A high strength bolt having excellent hydrogen embrittlement resistance according to either one of the claims 1 to 3, which further comprises:

higher than 0% and not higher than 2% of Cu and/or higher than 0% and not higher than 5% of Ni.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 00 1759

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	19 May 2006	Chebeleu, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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