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(54) **WIRE ROD HAVING SUPERIOR HYDROGEN DELAYED FRACTURE RESISTANCE, METHOD FOR MANUFACTURING SAME, HIGH STRENGTH BOLT USING SAME AND METHOD FOR MANUFACTURING BOLT**

(57) The present invention relates to a wire rod used in bolts for automobile engines, for example, and more specifically to a wire rod having an improved resistance to hydrogen delayed fracture, to a manufacturing method for same, to a bolt using same and a method for manufacturing the bolt. Provided are a high strength wire rod having a superior resistance to hydrogen delayed fracture and a method for manufacturing same, a high strength bolt using the wire rod and a method for manufacturing same, wherein the wire rod comprises, 0.3-0.7 wt% C, 0.05-2.0 wt% Si, 0.7-1.5 wt% Mn, 0.01-0.1 wt% Ni, and 30-70 ppm La, and the remainder thereof is comprised by Fe and inevitable impurities.

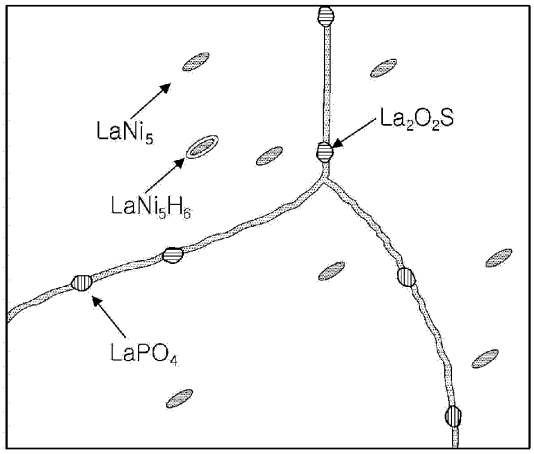

FIG. 1

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Description

[Technical Field]

[0001] The present disclosure relates to a wire rod used for automobile engine bolts and the like, and more particularly, to a wire rod having improved hydrogen delayed fracture resistance, a method for manufacturing the same, a high strength bolt using the same, and a method for manufacturing the bolt.

[Background Art]

[0002] In accordance with the recent trend for weight reductions and high functionalization in automobiles, requirements for driving parts, in particular, engine parts such as bolts and the like, to have high strength, have increased in order to reduce energy consumption. Currently used high strength bolts are manufactured to have a tensile strength of 1200 MPa through quenching and tempering processes, using alloyed steels such as SCM435, SCM440, and the like. However, in the bolts having a tensile strength of 1200 MPa or greater, since delayed fractures may be easily caused due to hydrogen, the uses of wire rods for manufacturing ultrahigh strength bolts remain inadequate.

[0003] According to a bolt manufacturing process, after performing wire drawing intended for sizing, through low temperature annealing, the drawn wire may be subjected to spheroidizing heat treatment, bolt-forming, quenching and tempering processes to finally obtain a steel having a single-phase structure composed of tempered martensite. Thus, strength of the bolt may be determined depending on composing, quenching, tempering and heat treatment processes performed thereon. However, the wire rod as a raw material needs to have as little strength as possible in order to facilitate bolt-forming.

[0004] In order to highly strengthen a steel having a single-phase structure composed of tempered martensite, the addition of alloying elements, in particular, carbon elements, has been known as the most effective method; however, the addition of carbon may rapidly increase a ductile to brittle transition temperature (DBTT) of a wire rod as well as increasing strength of the wire rod, and remarkably deteriorate hydrogen delayed fracture resistance. In addition thereto, work hardening may be increased, causing disadvantages in bolt-forming and a separate softening heat treatment may be required.

[0005] Bolts manufactured as described above may generally have a tempered martensite structure in which carbide precipitates are distributed in grain boundaries or gains and the basic material thereof has precipitates distributed in lath martensite. A main factor hindering the high strengthening of the basic material may be a degradation in delayed fracture resistance due to the introduction of hydrogen, and it has been known because the introduced hydrogen may deteriorate the strength of grain boundaries. In order to use existing tempered martensite in steel for high strength bolts, an operation for improving delayed fracture resistance may be required.

[0006] Thus, in order to achieve the high strengthening of bolts, improvements in delayed fracture resistance may be unavoidably required to increase critical delayed fracture strength, and to this end, a method of generating precipitates capable of trapping diffusible hydrogen or controlling a microstructure by adding certain elements while maximally suppressing phosphorus (P) and sulfide (S) brominating austenitic grain boundaries, and the like may be present.

[0007] The related art technologies for improving hydrogen delayed fracture resistance may include 1) corrosion suppression in steel, 2) minimization of an amount of introduced hydrogen, 3) suppression of diffusible hydrogen contributing to delayed fracture, 4) the use of steel having a high concentration of limited diffusible hydrogen contained therein, 5) minimization of tensile stress, 6) stress concentration reduction, 7) miniaturization of austenite grain boundary size, and the like. As a method of achieving improvements in hydrogen delayed fracture resistance, a method of implementing a high degree of alloying, or a surface coating method or a plating method for preventing the introduction of external hydrogen has been mainly used.

[0008] However, most inventions created domestically and internationally may have disadvantages such as high manufacturing costs and complex processes required therefor, and require excessively precise rolling and cooling conditions at the time of manufacturing steel. By way of example, in order to improve delayed fracture characteristics of a high strength wire rod having a tensile strength of 1600 MPa, technologies of adding 0.5 wt% of titanium (Ti), niobium (Nb), and vanadium (V), which are grain refinement elements, and then, adding corrosion resistance elements such as molybdenum (Mo), nickel (Ni), copper (Cu), cobalt (Co), and the like and carbide elements are present, but production costs required therefor may be significantly high. Furthermore, a method of improving hydrogen brittleness using ferrite structures extracted from grain boundaries is present, but the method does not include a chemical combination, and a product manufacturing cost may also increase due to the addition of a considerable amount of molybdenum (Mo).

[0009] In addition, a technology of improving delayed fracture characteristics of a high strength wire rod having a tensile strength of 1600 MPa or greater, using complete pearlite is present. However, in such a technology, 0.2 wt% or more of chrome needs to be added in order to improve tensile strength through wire drawing and to secure drawability during wire drawing intended for sizing after the production of a wire rod, and lead patenting for isothermal transformation

may necessarily be required. Thus, such a technology may have disadvantages such as high manufacturing costs and complex processes and have limitations such as the requirement for excessively precise rolling and cooling conditions at the time of manufacturing steel.

[0010] Moreover, through a technology of finally securing a tensile strength of 1200 to 1500 MPa using a ferrite-pearlite dual phase microstructure, the tensile strength may be secured without a final heat treatment, unlike in other technologies. However, since the technology basically aims at improving hydrogen delayed fracture resistance by adding a great quantity of molybdenum (Mo), it may be disadvantageous in terms of high manufacturing costs.

[0011] As described above, limitations to a decrease in hydrogen delayed fracture resistance as compared to an improvement in tensile strength in heat-treated and non heat-treated carbon steels having a tensile strength of 1200 MPa or greater have not yet been overcome, the securing of price competitiveness may not be available due to the addition of expensive alloying elements, and in particular, the stable securing of data regarding delayed fracture characteristics due to hydrogen may be defective.

[Disclosure]

[Technical Problem]

[0012] An aspect of the present disclosure provides a wire rod having superior hydrogen delayed fracture resistance while securing ultrahigh strength through a heat treatment, and a method for manufacturing the same.

[0013] An aspect of the present disclosure also provides a high strength bolt having superior hydrogen delayed fracture resistance using the wire rod, and a method for manufacturing the same.

[Technical Solution]

[0014] According to an aspect of the present disclosure, there is provided a wire rod having superior hydrogen delayed fracture resistance and including C: 0.3 to 0.7 wt%, Si: 0.05 to 2.0 wt%, Mn: 0.7 to 1.5 wt%, La: 30 to 70ppm, Ni: 0.01 to 0.1%, and a remainder configured of Fe and inevitable impurities.

[0015] According to another aspect of the present disclosure, there is provided a method for manufacturing a wire rod having superior hydrogen delayed fracture resistance, the method including: heating steel including C: 0.3 to 0.7 wt%, Si: 0.05 to 2.0 wt%, Mn: 0.7 to 1.5 wt%, La: 30 to 70ppm, Ni: 0.01 to 0.1%, and a remainder configured of Fe and inevitable impurities to a temperature of Ae3+150°C to Ae3+250°C; cooling the heated steel at a rate of 5 to 15°C/s and rolling the steel at a temperature of Ae3+50°C to Ae3+150°C to manufacture a wire rod; and cooling the rolled wire rod to 600 °C or less at a rate of 0.5 to 3°C/s.

[0016] According to another aspect of the present disclosure, there is provided a bolt including C: 0.3 to 0.7 wt%, Si: 0.05 to 2.0 wt%, Mn: 0.7 to 1.5 wt%, La: 30 to 70ppm, Ni: 0.01 to 0.1%, and a remainder configured of Fe and inevitable impurities, and having a tensile strength of 1200 MPa or greater and superior hydrogen delayed fracture resistance.

[0017] According to another aspect of the present disclosure, there is provided a method for manufacturing a bolt having superior hydrogen delayed fracture resistance, the method including: heating steel including C: 0.3 to 0.7 wt%, Si: 0.05 to 2.0 wt%, Mn: 0.7 to 1.5 wt%, La: 30 to 70ppm, Ni: 0.01 to 0.1%, and a remainder configured of Fe and inevitable impurities to a temperature of Ae3+150°C to Ae3+250°C; cooling the heated steel at a rate of 5 to 15°C/s and rolling the steel at a temperature of Ae3+50°C to Ae3+150°C to manufacture a wire rod; cooling the rolled wire rod to 600°C or less at a rate of 0.5 to 3°C/s; and bolt-forming using the cooled wire rod; performing a heat treatment on the formed bolt at a temperature of 850 to 950°C; and performing quenching after the heat treatment, and then performing tempering at a temperature of 300 to 500°C.

[Advantageous Effects]

[0018] The wire rod according to the present disclosure may be a high strength wire rod used for the coupling of automobile components or used in such automobile components, and the method of manufacturing the wire rod may be advantageous in that a wire rod having high strength of 1200 MPa to 2000 MPa and superior hydrogen delayed fracture resistance, even in a case in which a tiny amount of lanthanum and nickel is added or even in a case in which a martensite microstructure is present after the final heat treatment, may be manufactured with low manufacturing costs.

[0019] In accordance with the development of a wire rod for bolts having superior hydrogen delayed fracture resistance and high strength, the stability of a steel structure may be increased due to a reinforcement of coupling force and a reduction of vacancies in a coupling part at the time of coupling the bolts, and an amount of steel used may be reduced due to a decrease in the number of coupled bolts. In addition, in terms of automobile components, the development of the wire rod for bolts as described above may contribute to lightening of the automobile components. Due to the lightening of automobile components, various automobile assembling device designs may be enabled and compactness of auto-

mobile assembling devices may be allowed.

[Description of Drawings]

[0020]

FIG. 1 is a schematic view illustrating a microstructure of a wire rod according to an exemplary embodiment of the present disclosure.
FIG. 2 is a schematic view illustrating hydrogen trapping of a molybdenum (Mo) precipitate in the case of the addition of Mo according to the related art.
FIG. 3 is a schematic view illustrating hydrogen trapping of a precipitate contained in the wire rod according to the exemplary embodiment of the present disclosure.
FIG. 4 is a view illustrating a crystal structure of the precipitate of FIG. 3.

[Best Mode]

[0021] Hereinafter, exemplary embodiments of the present disclosure will be described in detail.

[0022] First, a wire rod according to an exemplary embodiment of the present disclosure will be described in detail. Here, a compositional range of the wire rod according to the exemplary embodiment of the present disclosure will be described (hereinafter, referred to as weight percentage (wt%)).

[0023] Carbon (C) may be included in the wire rod in an amount of 0.3 to 0.7 wt%. When carbon (C) is included in an amount exceeding 0.7 wt%, although the wire rod may be frequently used in the form of a high carbon wire rod formed using common cold wire drawing, in a case in which the wire rod is subjected to a heat treatment suggested in the exemplary embodiment of the present disclosure, film shaped carbides may be frequently eluted in austenite grain boundaries to thereby deteriorate hydrogen delayed fracture resistance. Thus, an amount of carbon (C) exceeding 0.7 wt% may not be preferable. Meanwhile, when carbon (C) is included in an amount less than 0.3 wt%, since tensile strength of a bolt may be insufficiently secured through quenching and tempering heat treatments, carbon (C) may be added in an amount of 0.3 wt% or greater in order to secure a sufficient degree of strength.

[0024] Silicon (Si) may be included in the wire rod in an amount of 0.05 to 2.0 wt%. When silicon (Si) is included in an amount exceeding 2.0 wt%, a work hardening phenomenon may be rapidly generated during a cold forging process for manufacturing bolts to deteriorate processability. When silicon (Si) is included in an amount less than 0.05 wt%, a sufficient degree of strength may not be secured and spheroidization of cementite may also be adversely affected.

[0025] Manganese (Mn) may be included in the wire rod in an amount of 0.7 to 1.5 wt%. Manganese (Mn), an element forming a substitutional solid solution in a base structure to perform solid solution reinforcement, may be very useful in high tension bolt characteristics. When manganese (Mn) is included in an amount exceeding 1.5 wt%, a heterogeneous structure caused by manganese segregation may have a negative influence on bolt characteristics, rather than having solid solution reinforcement effects. That is, during the coagulation of steel, macroscopic and microscopic segregation may be easily generated according to a segregating device, and manganese (Mn) may aggravate a segregation area due to the diffusion coefficient thereof relatively being lower than that of other elements and the consequent hardenability improvements may be a main factor generating a core low temperature structure (for example, core martensite). That is, an increase in local quenching properties and the formation of a segregation area caused by manganese segregation during casting may intensify dual phase properties of the structure.

[0026] Meanwhile, when manganese (Mn) is included in an amount less than 0.7 wt%, the segregation area may be barely affected by the manganese segregation, but tensile strength of a final product may not be secured through solid solution reinforcement. That is, when manganese (Mn) is included in an amount less than 0.7 wt%, improvements in quenching and permanent deformation resistance may be insufficient due to insufficient solid solution reinforcement.

[0027] Nickel (Ni) may be included in the wire rod in an amount of 0.01 to 0.1 wt%. Nickel (Ni) may be a very important element forming a compound within a grain boundary, together with lanthanum (La). Thus, when nickel (Ni) is included in an amount less than 0.01 wt%, an effective compound, in particular, precipitates, may not be completely generated, thereby leading to an inability to improve hydrogen delayed fracture resistance. When nickel (Ni) is included in an amount exceeding 0.1 wt%, the amount of the remaining austenite may be increased to degrade impact toughness and manufacturing costs may be increased due to an excessive amount of nickel.

[0028] Lanthanum (La) may be included in the wire rod in an amount of 0.003 to 0.007 wt% (30~70ppm). Lanthanum (La) may be a very important element forming a compound within a grain boundary, together with Nickel (Ni) and decreasing phosphorous and sulfur segregated in the grain boundary. Thus, when lanthanum (La) is included in an amount less than 30ppm, the compound may not be effectively formed and the removal of phosphorus and sulfur segregated in the grain boundary may not be facilitated. Thus, the securing of tensile strength may be enabled but superior hydrogen delayed fracture resistance may not be expected. On the other hand, when lanthanum (La) is included

in an amount exceeding 70ppm, since manufacturing costs may be increased and the hydrogen delayed fracture resistance may not be improved due to an excessive amount of lanthanum, the upper limit of the amount of added lanthanum may be 70ppm.

[0029] The remainder may include iron (Fe) and inevitable impurities. In addition to the composition described above, the addition of effective elements may not be excluded.

[0030] The wire rod according to the exemplary embodiment of the present invention may include a lanthanum (La)-based, a nickel (Ni)-based, or a LaNi-based precipitate. Types of the precipitate are not particularly limited, but examples thereof may include $LaNi_5$, $LaPO_4$, La_2O_2S and the like. The precipitate may be formed in a grain or a grain boundary of a microstructure and trap hydrogen introduced into the grain or the grain boundary to prevent the introduced hydrogen from deteriorating strength of the grain boundary, thereby improving hydrogen delayed fracture resistance.

[0031] FIG. 1 schematically illustrates a state in which precipitates are distributed by observing the microstructure of the wire rod according to the exemplary embodiment of the present disclosure. As illustrated in FIG. 1, it may be confirmed that precipitates of $LaNi_5$, $LaPO_4$, and La_2O_2S are distributed in a grain or a grain boundary of the microstructure, and a compound of $LaNi_5H_6$ is present due to the trapping of hydrogen.

[0032] Meanwhile, hydrogen trapping effects due to the precipitates according to the exemplary embodiment of the present disclosure may be significantly superior, as compared to the related art technology intended to improve hydrogen delayed fracture resistance through molybdenum (Mo). FIG. 2 schematically illustrates hydrogen trapping effects using a molybdenum (Mo) precipitate according to the related art, and the molybdenum (Mo) precipitate may be intended to trap introduced hydrogen within an interface between the precipitate and a grain to thereby improve hydrogen delayed fracture resistance. However, in FIG. 3, schematically illustrating hydrogen trapping effects due to the precipitate according to the exemplary embodiment of the present disclosure, the precipitate according to the exemplary embodiment of the present disclosure may allow for the formation of a compound (for example, $LaNi_5H_6$) including introduced hydrogen, rather than confining the hydrogen to a surface of the precipitate, such that hydrogen present in steel may be completely confined to thereby improve hydrogen delayed fracture resistance. Thus, in the case of FIG. 2, a defect in which hydrogen is separated from the surface of the precipitate may be present, but such a defect may be fundamentally extinct, such that superior hydrogen delayed fracture resistance may be obtained, in the embodiment of the present disclosure. FIG. 4 illustrates a crystal structure of $LaNi_5H_6$ of FIG. 3, and it can be confirmed that the compound of $LaNi_5H_6$ may have a structure capable of storing a considerable amount of hydrogen therein.

[0033] An aspect ratio of the precipitate may be 1.2 to 2.0. When the aspect ratio of the precipitate is less than 1.2, the securing of the compound may rarely be allowed due to the crystal structure. When the aspect ratio of the precipitate exceeds 2.0, the precipitate may be easily broken. In a case in which the precipitate is broken in a material, continuity thereof with a base may be deficient and micro-voids may be generated, thereby causing defects. Thus, breakage of the wire rod may be caused and expected hydrogen delayed fracture resistance may not be secured.

[0034] Meanwhile, in terms of a size of the precipitate, a circular-equivalent diameter of the precipitate may be 100 to 400nm. When the diameter is less than 100nm, the size of the precipitate may be excessively small, an amount of hydrogen trapped in the precipitate may be reduced, whereby effective hydrogen trapping effects may not be secured. When the diameter exceeds 400nm, and is significantly large, since the number of precipitates distributed per unit area may be reduced, a decrease in a surface area of the precipitates in the overall steel may result, thereby reducing hydrogen trapping effects, the upper limit of the diameter of the precipitate may be 400 nm.

[0035] Hereinafter, a method for manufacturing a wire rod according to an exemplary embodiment of the present disclosure will be described in detail.

[0036] In order to manufacture the wire rod according to the exemplary embodiment of the present disclosure, steel satisfying the composition described above may be heated to a temperature of Ae3+150°C to Ae3+250°C. The heating to the temperature may be intended to maintain an austenite single phase, and in a range of the temperature, austenite grain coarsening may not be generated and the remaining segregation, carbides and inclusions may be effectively dissolved. When the temperature exceeds Ae3+250°C, an austenite grain may be significantly coarse, such that a final microstructure formed after cooling may be highly coarse, resulting in an inability to secure a high strength wire rod having a high degree of toughness. Meanwhile, when the heating temperature is less than Ae3+150°C, heating effects may not be obtained and consequently, the heating temperature may be Ae3+150°C to Ae3+250°C.

[0037] The heating may be undertaken for 30 minutes to one and a half hours. When the heating is performed for less than 30 minutes, the entire temperature may not be uniform. When the heating is performed for more than one and a half hours, possibility that the austenite grain may be coarse may be higher and productivity may be significantly reduced.

[0038] The heated steel may be cooled and be subjected to hot rolling. The cooling may be performed at a cooling rate of 5 to 15°C/s and the rolling may be performed at a temperature of Ae3+50°C to Ae3+150°C, to thereby manufacture a wire rod.

[0039] The cooling may be intended to perform controlling aiming at minimizing the transformation of the microstructure. When the cooling rate is less than 5°C/s before the rolling, productivity may be decreased, an additional device may be required in order to maintain a slow cooling rate, and further, strength and toughness of the wire rod may be deteriorated

after the hot rolling, similarly to the case in which the heating is maintained for long hours. On the other hand, when the cooling rate exceeds 15°C/s, since driving force of the transformation in steel before the rolling may be increased, the possibility that a new microstructure may emerge during the rolling may be increased, such that a lower rolling temperature may need to be reset.

[0040] In addition, the rolling temperature may be a temperature at which the emergence of a microstructure caused by the transformation during the rolling may be inhibited, recrystallization may not be generated, and only sizing rolling may be enabled. When the rolling temperature is less than Ae3+50°C, it may be close to the dynamic recrystallization temperature, such that the securing of the microstructure may be unavailable and general soft ferrite may be highly secured. Meanwhile, when the rolling temperature is greater than Ae3+150°C, since reheating may be required after the cooling, the upper limit of the rolling temperature may be set as described above.

[0041] The wire rod manufactured through the rolling as described above may be cooled to 600 °C or less at a cooling rate of 0.5 to 3°C/s. The cooling rate may refer to a cooling rate at which the diffusion of carbon may be suppressed by the addition of manganese, and the wire rod may be effectively generated while pearlite is incompletely generated and a sufficient area fraction is secured. When the cooling rate is less than 0.5°C/s, the cooling rate may be extremely low, thereby degrading productivity to a degree to which actual work becomes infeasible. When the cooling rate exceeds 3°C/s, hardenability may be improved due to overlapping effects of the added elements, such that ferrite-pearlite transformation may be delayed and a low temperature structure such as martensite or bainite may be generated.

[0042] Hereinafter, a bolt according to an exemplary embodiment of the present disclosure and a method for manufacturing the same will be described in detail.

[0043] The bolt manufactured using the wire rod according to the embodiment of the present disclosure may have ultrahigh strength and at the same time, may have superior hydrogen delayed fracture resistance due to the precipitate. The bolt according to the exemplary embodiment of the present disclosure may have ultrahigh strength of 1200 MPa or greater and at the same time, may have superior hydrogen delayed fracture resistance.

[0044] The manufacturing method of a wire rod having tensile strength of 1200 MPa or greater may be performed according to the following operations. First, bolt-forming may be performed using the wire rod according to the embodiment of the present disclosure, and a heat treatment may be performed on the formed bolt at a temperature of 850 to 950°C. The heat treatment may be intended to achieve homogenization of the structure through austenizing. When the temperature is less than 850°C, a sufficient amount of homogenization may not be performed, while when the temperature is greater than 950°C, no further effects derived from an increase in temperature may be secured and ductility may be deteriorated due to the coarsening of grains. Thus, the upper limit of the temperature may be 950°C.

[0045] After the heat treatment, quenching may be performed and tempering may be undertaken at a temperature of 300 to 500°C. The structure homogenized through rapid cooling may form a low temperature transformation structure such as a martensite structure to thereby improve strength of the bolt.

[0046] The tempering may be intended to control strength and improve brittleness by removing residual stress generated due to the rapid cooling. When the temperature is less than 300°C, sufficient removal of residual stress may be difficult and rather, brittleness may be generated as a temper brittleness phenomenon. Thus, the temperature may be 300°C or greater. When the temperature exceeds 500°C, the strength may be reduced due to an excessive heat treatment, thereby leading to an inability to secure a required level of strength. Thus, the tempering may be undertaken at a temperature of 300 to 500°C.

[0047] The method for manufacturing the bolt may be intended to secure a required level of strength by applying a common heat treatment thereto. The common heat treatment may be applied by controlling time and temperature in order to secure strength required by a person having ordinary skill in the art and the present disclosure is not particularly limited thereto.

[Mode for Disclosure]

[0048] Hereinafter, examples of the present disclosure will be described in detail. The following examples are merely provided for understanding of the present disclosure, and the present disclosure is not limited thereto.

(Example 1)

[0049] Steels having compositions of Table 1 and Ae3 temperature were manufactured and then, wire rods were manufactured using the steels under conditions of Table 2. Bolts were manufactured using the wire rods manufactured as above. In this case, heat treatment conditions in a manufacturing process of the bolts were described in Table 2.

[0050] Tensile strength and hydrogen delayed fracture resistance of the respective bolts manufactured above were measured and the results thereof are shown in Table 3. The hydrogen delayed fracture resistance of the respective bolts were measured in such a manner that tensile strengths corresponding to about 0.9 times those of tensile strength of the respective bolts, measured in a state in which the respective bolts were immersed in a test solution having an

acidity of about 2 and configured of H_2O: 2000cc, CH3COOH: 80ml, and NaCl: 100g were imparted to the bolts and then, hours after which the respective specimens were broken, were measured. Through the test, in a case in which the specimen was maintained unbroken for 100 hours or more, it was estimated that resistance to hydrogen delayed fracture was excellent.

Table 1

Classification	C	Si	Mn	La	Ni	Remainder	Ae3 temperature
Comparative Example 1	0.01	0.02	0.55	0.001	0.06	-	886
Comparative Example 2	0.82	0.5	1.2	0.05	0.06	-	856
Comparative Example 3	0.37	0.02	0.50	-	-	Mo 0.27	810
Comparative Example 4	0.35	0.03	0.52	-	-	Mo 0.64	826
Comparative Example 5	0.40	0.02	0.55	-	-	Mo 0.85	823
Comparative Example 6	0.39	0.18	0.78	-	0.09	-	820
Comparative Example 7	0.44	0.55	1.16	0.004	-	-	825
Comparative Example 8	0.45	0.42	1.18	0.001	0.06	-	824
Comparative Example 9	0.38	0.02	0.56	0.01	0.06	-	811
Comparative Example 10	0.46	0.51	1.2	0.007	0.005	-	821
Comparative Example 11	0.45	0.52	1.2	0.007	0.15	-	824
Inventive Example 1	0.38	0.05	0.7	0.005	0.06	-	820
Inventive Example 2	0.45	0.5	1.2	0.007	0.04	-	821
Inventive Example 3	0.62	0.5	0.83	0.004 8	0.06	-	785

Table 2

Classification	Wire rod manufacturing process				Bolt processing conditions	
	Steel heating temperature and hour (°C, Minutes)	Cooling Rate (°C/s)	Rolling Temperature (°C)	Cooling Rate after rolling (°C/s)	Heating Temperature (°C)	Tempering temperature (°C)
Comparative Example 1	1082, 80	9.7	989	1.3	870	350
Comparative Example 2	1090, 62	13.2	956	0.2	870	350
Comparative Example 3	1067, 72	11.8	969	2.1	870	350
Comparative Example 4	1081, 81	12.6	975	2.2	870	350
Comparative Example 5	1078, 69	13.3	958	1.9	870	450
Comparative Example 6	1015, 71	11.9	978	0.5	870	350
Comparative Example 7	1065, 65	10.2	988	0.9	870	450
Comparative Example 8	1111, 88	9.6	990	1.5	870	450

(continued)

Classification	Wire rod manufacturing process				Bolt processing conditions	
	Steel heating temperature and hour (°C, Minutes)	Cooling Rate (°C/s)	Rolling Temperature (°C)	Cooling Rate after rolling (°C/s)	Heating Temperature (°C)	Tempering temperature (°C)
Comparative Example 9	1093, 78	13.9	991	2.3	870	350
Comparative Example 10	1038, 79	10.2	972	0.8	870	450
Comparative Example 11	1082, 82	11.7	965	0.3	870	450
Inventive Example 1	1053, 82	12.4	978	0.6	870	450
Inventive Example 2	1065, 89	10.2	981	1.1	870	450
Inventive Example 3	1071, 79	9.1	980	1.7	870	450

Table 3

Classification	Tensile strength (MPa)	Breaking time (H)											
		10	20	30	40	50	60	70	80	90	100	200	300
Comparative Example 1	1012	×	×	×	×	×	×	×	×	×	×	○	-
Comparative Example 2	1760	○	-	-	-	-	-	-	-	-	-	-	-
Comparative Example 3	1390	×	×	×	○	-	-	-	-	-	-	-	-
Comparative Example 4	1420	×	×	×	×	×	○	-	-	-	-	-	-
Comparative Example 5	1435	×	×	×	×	×	×	×	×	○	-	-	-
Comparative Example 6	1320	×	×	×	×	×	×	○	-	-	-	-	-
Comparative Example 7	1290	×	×	×	×	×	×	×	○	-	-	-	-
Comparative Example 8	1360	×	×	×	×	×	×	×	×	○	-	-	-
Comparative Example 9	1590	×	×	×	×	×	×	×	×	×	×	×	×
Comparative Example 10	1365	×	×	×	×	×	○	-	-	-	-	-	-
Comparative Example 11	1610	×	×	×	×	×	×	×	×	×	×	×	×
Inventive Example 1	1250	×	×	×	×	×	×	×	×	×	×	×	×
Inventive Example 2	1680	×	×	×	×	×	×	×	×	×	×	×	×
Inventive Example 3	2019	×	×	×	×	×	×	×	×	×	×	×	×
○: Breakage Occurrence, ×: Breakage Non-Occurrence													

[0051] In a case in which conditions of the present disclosure were satisfied, at the time of manufacturing the bolt, it could be confirmed that the bolt had high strength of 1200 MPa or greater, while having superior hydrogen delayed fracture resistance. However, comparative examples 9 and 10 were classified as comparative examples because they had sufficient strength and hydrogen delayed fracture resistance, but were not preferable in terms of economical feasibility due to the addition of an excessive amount of La and Ni.

[0052] Meanwhile, in a case in which carbon (C) was included in an excessively low amount as in comparative example

1, it could be confirmed that a sufficient amount of strength was not secured, and in a case in which carbon (C) was included in an excessively high amount as in comparative example 2, it could be confirmed that hydrogen delayed fracture resistance was significantly low. In the cases of comparative examples 3 to 5 having molybdenum (Mo) added therein, it could be confirmed that breakage occurred before 100 hours, the securing of sufficient hydrogen delayed fracture resistance was difficult. In the case in which only one of La and Ni was added, as in comparative examples 6 and 7, sufficient hydrogen delayed fracture resistance was not secured.

[0053] In a case in which the addition of La or Ni does not reach a set range of the present disclosure, as in examples 8 and 9, it could be confirmed that sufficient hydrogen delayed fracture resistance was not secured.

(Example 2)

[0054] In order to determine hydrogen delayed fracture resistance depending on a size and an aspect ratio of a lanthanum (La)-based, a nickel (Ni)-based, or a LaNi-based precipitate, the size and the aspect ratio of the precipitate were varied through a heat treatment in the cases of inventive examples 1 to 3.

[0055] After the size and the aspect ratio of the precipitate were varied as described above, hydrogen delayed fracture resistance was measured in the same manner as that of the foregoing example 1 and the results thereof were shown in Table 4.

Table 4

Classification	Average size of precipitate	Aspect ratio of precipitate	Breaking Time (H)												Remark
			10	20	30	40	50	60	70	80	90	100	200	300	
Inventive Example 1	320nm	1.7	×	×	×	×	×	×	×	×	×	×	×	×	Inventive material
Inventive Example 2	220nm	1.2	×	×	×	×	×	×	×	×	×	×	×	×	Inventive material
Inventive Example 3	195nm	1.9	×	×	×	×	×	×	×	×	×	×	×	×	Inventive material
Inventive Example 1-1	364nm	1.05	×	×	×	×	×	×	×	×	×	○	-	-	Comparative material
Inventive Example 2-1	280nm	3.2	×	×	○	-	-	-	-	-	-	-	-	-	Comparative material
Inventive Example 3-1	97nm	1.8	×	×	×	○	-	-	-	-	-	-	-	-	Comp arative material
Inventive Example 3-2	532nm	1.55	×	×	×	×	×	×	×	×	○	-	-	-	Comparative material
○: Breakage Occurrence, ×: Breakage Non-Occurrence															

[0056] As can be seen in Table 4, it could be confirmed that when the aspect ratio of the precipitate was outside the range of the present disclosure, hydrogen delayed fracture resistance was low.

Claims

1. A wire rod having superior hydrogen delayed fracture resistance and comprising C: 0.3 to 0.7 wt%, Si: 0.05 to 2.0 wt%, Mn: 0.7 to 1.5 wt%, La: 30 to 70ppm, Ni: 0.01 to 0.1%, and a remainder configured of Fe and inevitable impurities.

2. The wire rod of claim 1, wherein the wire rod includes a lanthanum (La)-based, a nickel (Ni)-based, or a LaNi-based precipitate.

3. The wire rod of claim 2, wherein an aspect ratio of the precipitate is 1.2 to 2.0.

4. The wire rod of claim 2, wherein an average circular-equivalent diameter of the precipitate is 100 to 400nm.

5. The wire rod of claim 2, wherein the precipitate is at least one of $LaNi_5$, $LaPO_4$ and La_2O_2S .

6. A method for manufacturing a wire rod having superior hydrogen delayed fracture resistance, the method comprising:

   heating steel including C: 0.3 to 0.7 wt%, Si: 0.05 to 2.0 wt%, Mn: 0.7 to 1.5 wt%, La: 30 to 70ppm, Ni: 0.01 to 0.1%, and a remainder configured of Fe and inevitable impurities to a temperature of Ae3+150°C to Ae3+250°C;
   cooling the heated steel at a rate of 5 to 15°C/s and rolling the steel at a temperature of Ae3+50°C to Ae3+150°C to manufacture a wire rod; and
   cooling the rolled wire rod to 600 °C or less at a rate of 0.5 to 3°C/s.

7. The method of claim 6, wherein the heating is performed for 30 minutes to one and a half hours.

8. A bolt comprising C: 0.3 to 0.7 wt%, Si: 0.05 to 2.0 wt%, Mn: 0.7 to 1.5 wt%, La: 30 to 70ppm, Ni: 0.01 to 0.1%, and a remainder configured of Fe and inevitable impurities, and having a tensile strength of 1200 MPa or greater and superior hydrogen delayed fracture resistance.

9. The bolt of claim 8, wherein a microstructure of the bolt includes a lanthanum (La)-based, a nickel (Ni)-based, or a LaNi-based precipitate having an aspect ratio of 1.2 to 2.0.

10. The bolt of claim 9, wherein the aspect ratio of the precipitate is 1.2 to 2.0.

11. The bolt of claim 9, wherein an average circular-equivalent diameter of the precipitate is 100 to 400nm.

12. The bolt of claim 9, wherein the precipitate is at least one of $LaNi_5$, $LaPO_4$ and La_2O_2S.

13. A method for manufacturing a bolt having superior hydrogen delayed fracture resistance, the method comprising:

   heating steel including C: 0.3 to 0.7 wt%, Si: 0.05 to 2.0 wt%, Mn: 0.7 to 1.5 wt%, La: 30 to 70ppm, Ni: 0.01 to 0.1%, and a remainder configured of Fe and inevitable impurities to a temperature of Ae3+150°C to Ae3+250°C;
   cooling the heated steel at a rate of 5 to 15°C/s and rolling the steel at a temperature of Ae3+50°C to Ae3+150°C to manufacture a wire rod;
   cooling the rolled wire rod to 600 °C or less at a rate of 0.5 to 3°C/s; and
   bolt-forming using the cooled wire rod;
   performing a heat treatment on the formed bolt at a temperature of 850 to 950°C; and
   performing quenching after the heat treatment, and then performing tempering at a temperature of 300 to 500°C.

14. The method of claim 13, wherein the heating is performed for 30 minutes to one and a half hours.

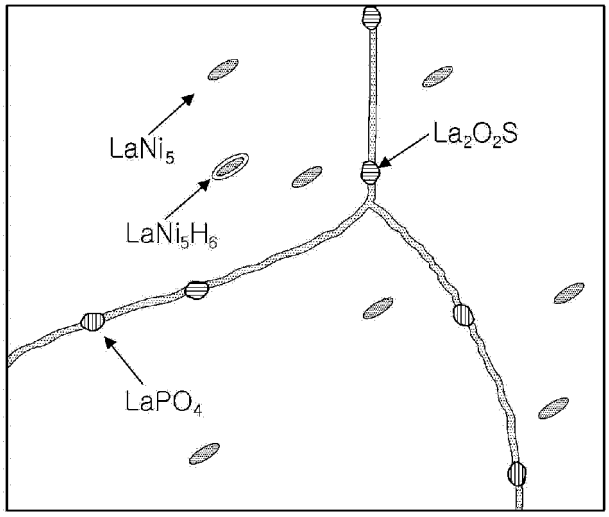

FIG. 1

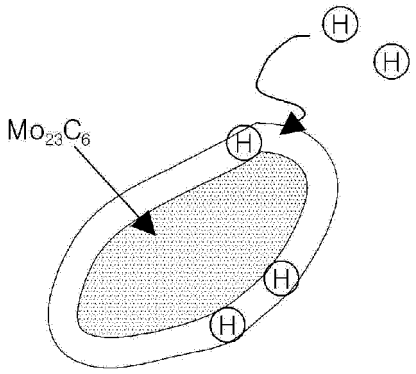

FIG. 2

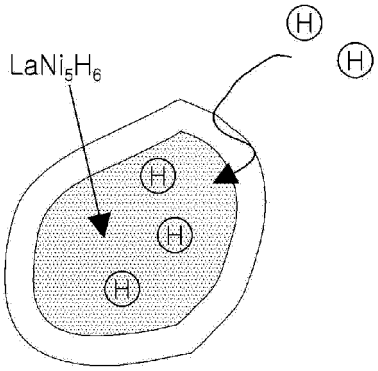

FIG. 3

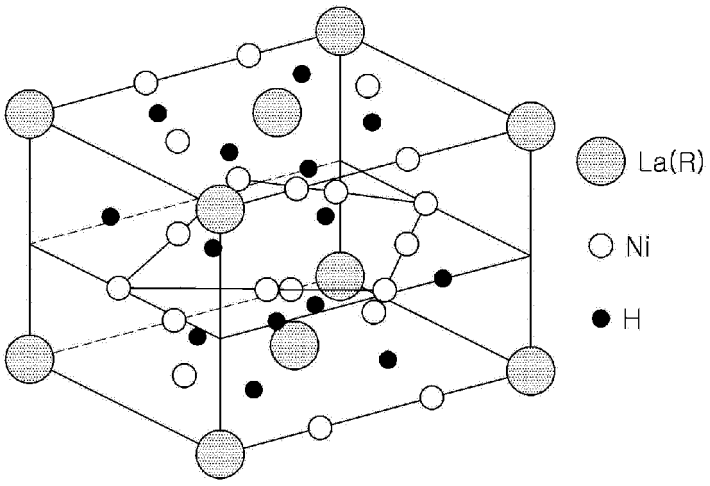

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2012/003757

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i, C21D 8/06(2006.01)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)

C22C 38/00; C21C 5/28; C21D 8/06; C21D 8/00; C21C 7/06; C21D 9/00; C22C 38/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models: IPC as above
Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & Keywords: wire rod, La, precipitate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2008-0106562 A (KABUSHIKI KAISHA KOBE SEIKO SHO) 08 December 2008 See abstract and claims 1 - 4.	1-2
A	KR 10-2008-0106562 A (KABUSHIKI KAISHA KOBE SEIKO SHO) 08 December 2008 See abstract and claims 1 - 4.	3-14
A	KR 10-2011-0013889 A (POSCO) 10 February 2011 See abstract and claims 1 - 13.	1-14
A	KR 10-2009-0071164 A (POSCO) 01 July 2009 See abstract and claims 1 - 5.	1-14
A	JP 07-173577 (KOBE STEEL LTD) 11 July 1995 See abstract and claims 1 - 8.	1-14

☐ Further documents are listed in the continuation of Box C. ☒ 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
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"T" 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
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"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	Date of mailing of the international search report
29 OCTOBER 2012 (29.10.2012)	**01 NOVEMBER 2012 (01.11.2012)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2012/003757

Patent document cited in search report	Publication date	Patent family member	Publication date
KR 10-2008-0106562 A	08.12.2008	CN 101389772 A	18.03.2009
		JP 04-069150 B2	02.04.2008
		JP 2007-291496 A	08.11.2007
		US 2009-0038439 A1	12.02.2009
		WO 2007-114100 A1	11.10.2007
KR 10-2011-0013889 A	10.02.2011	CN 102471851 A	23.05.2012
		US 2012-0118443 A1	17.05.2012
		WO 2011-016676 A2	10.02.2011
		WO 2011-016676 A3	10.02.2011
KR 10-2009-0071164 A	01.07.2009	NONE	
JP 07-173577 A	11.07.1995	CA 2135035 A1	05.05.1995
		CA 2135035 C	20.07.1999
		DE 69410223 D1	18.06.1998
		DE 69410223 T2	04.02.1999
		EP 0657557 A1	14.06.1995
		EP 0657557 B1	13.05.1998
		ES 2116506 T3	16.07.1998
		JP 02-932943 B2	28.05.1999
		JP 2932943 B2	09.08.1999
		US 05508002A A	16.04.1996
		US 05846344A A	08.12.1998

Form PCT/ISA/210 (patent family annex) (July 2009)