



(11) **EP 4 265 766 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
25.10.2023 Bulletin 2023/43

(21) Application number: **21907056.2**

(22) Date of filing: **14.12.2021**

(51) International Patent Classification (IPC):
C22C 38/00 (2006.01) **C22C 38/02** (2006.01)
C22C 38/04 (2006.01) **C22C 38/14** (2006.01)
C21D 9/52 (2006.01) **C21D 8/06** (2006.01)

(52) Cooperative Patent Classification (CPC):
C21D 8/06; C21D 9/52; C22C 38/00; C22C 38/02;
C22C 38/04; C22C 38/14

(86) International application number:
PCT/KR2021/018977

(87) International publication number:
WO 2022/131752 (23.06.2022 Gazette 2022/25)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR

Designated Extension States:
BA ME

Designated Validation States:
KH MA MD TN

(30) Priority: **18.12.2020 KR 20200178274**

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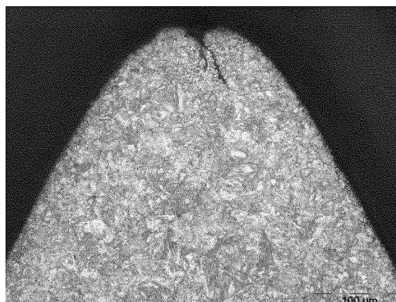
(54) **WIRE ROD AND PARTS WITH IMPROVED DELAYED FRACTURE RESISTANCE, AND METHODS FOR MANUFACTURING SAME**

(57) Disclosed are wire rods and parts with improved delayed fracture resistance, and methods for manufacturing the same. The wire rod with improved delayed fracture resistance according to the present disclosure contains, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance, and satisfies formula 1.

$$\text{[Formula 1]} \quad 2.0 \leq 5.5 \times [\text{Si}] + [\text{Mn}] \leq 2.4$$

(In formula 1, [Si] and [Mn] represent the contents (wt%) of the corresponding elements.)

[FIG. 1]



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Description

[Technical Field]

5 **[0001]** The present disclosure relates to a wire rod and a part with improved delayed fracture resistance, and methods for manufacturing the same, more specifically to a wire rod and a part that can be used in fastening bolts, etc. of automobiles and structures exposed to various stress and corrosion environments, and methods for manufacturing the same.

10 [Background Art]

[0002] High strength is required for wire rods which are used for fastening bolts, etc. for automobiles and structures with the weight reduction and miniaturization of automobiles and structures. In general, cold working, grain refinement, martensite strengthening, precipitation strengthening, etc. are utilized to increase the strength of steel materials.

15 **[0003]** However, the dislocations, grain boundaries, martensite lath boundaries, fine precipitate boundaries, used for strengthening lead to inferior delayed fracture by acting as hydrogen traps in steel materials. For this reason, the delayed fracture becomes inferior in high-strength bolts with a tensile strength of 1 GPa or higher.

[0004] In order to solve this problem, Cr-Mo alloy steel with Mo added was used in steel for high-strength bolts with a tempered martensite structure having a tensile strength of 1 GPa or higher. But, there have been attempts to replace the Cr-Mo steel with Cr-B steel in order to respond to the need for cost reduction with the development of the bolt manufacturing technology. As a result, cost reduction was realized by using Cr-B steel for bolts used in structures with no significant impact on safety. Then, after its safety was confirmed, the Cr-B steel is used for some fastening bolts of automobiles.

20 **[0005]** Furthermore, in the automobile industry, there is a need to develop a material for bolts that can reduce cost more than the Cr-B steel. In order to respond to this need, technological development has been conducted recently to apply Mn-B steel utilizing Mn, which is cheaper than Cr, for high-strength bolts of 1 GPa or higher.

[0006] However, since Mn causes high solid solution strengthening in the ferrite matrix as compared to Cr, the Mn-B steel may cause cracking in the thread part of the bolt. Therefore, the steel with a high content of Mn, which is added to manufacture a high-strength bolt of 1 GPa or higher, is difficult to be used for a high-strength bolt because delayed fracture may occur in the bolt thread part due to cracking.

[Disclosure]

[Technical Problem]

35 **[0007]** In an aspect, the present disclosure is directed to providing a wire rod with improved delayed fracture resistance for a high-strength bolt, by optimizing the solid solution strengthening effect of Mn-B steel and improving formability through control of alloy elements, the bolt and methods for manufacturing the same.

40 [Technical Solution]

[0008] A wire rod with improved delayed fracture resistance according to an exemplary embodiment of the present disclosure contains, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance, and satisfies formula 1.

$$\text{[Formula 1]} \quad 2.0 \leq 5.5 \times [\text{Si}] + [\text{Mn}] \leq 2.4$$

50 **[0009]** In formula 1, [Si] and [Mn] represent the contents (wt%) of the corresponding elements.

[0010] In another exemplary embodiment of the present disclosure, the wire rod may satisfy formula 2.

$$\text{[Formula 2]} \quad 1.0 < [\text{Ti}] / 3.42[\text{N}] < 2.0$$

55 **[0011]** In formula 2, [Ti] and [N] represent the contents (wt%) of the corresponding elements.

[0012] In another exemplary embodiment of the present disclosure, the size of TiN inclusions may be 15 μm or smaller.

[0013] A method for manufacturing a wire rod with improved delayed fracture resistance according to an exemplary

embodiment of the present disclosure includes: a step of finish-rolling a steel material containing, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance and satisfying formula 1 at 880-980 °C; and a step of winding at 830-930 °C.

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$$\text{[Formula 1]} \quad 2.0 \leq 5.5 \times [\text{Si}] + [\text{Mn}] \leq 2.4$$

[0014] In formula 1, [Si] and [Mn] represent the contents (wt%) of the corresponding elements.

10 **[0015]** In another exemplary embodiment of the present disclosure, the steel material may satisfy formula 2.

$$\text{[Formula 2]} \quad 1.0 < [\text{Ti}] / 3.42[\text{N}] < 2.0$$

15 **[0016]** In formula 2, [Ti] and [N] represent the contents (wt%) of the corresponding elements.

[0017] A method for manufacturing a part with improved delayed fracture resistance according to an exemplary embodiment of the present disclosure includes: a step of drawing a wire rod manufactured according to the present disclosure; a step of spheroidization heat-treating the drawn wire rod at 745-770 °C; a step of heating the spheroidization heat-treated drawn wire rod at 870-940 °C; a step of quenching the spheroidization heat-treated drawn wire rod at 50-80 °C; and a step of tempering the quenched part at 400-600 °C.

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[0018] A part with improved delayed fracture resistance according to an exemplary embodiment of the present disclosure contains, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance and satisfies formula 1.

25

$$\text{[Formula 1]} \quad 2.0 \leq 5.5 \times [\text{Si}] + [\text{Mn}] \leq 2.4$$

[0019] In formula 1, [Si] and [Mn] represent the contents (wt%) of the corresponding elements.

30 **[0020]** In another exemplary embodiment of the present disclosure, the part satisfies formula 2.

$$\text{[Formula 2]} \quad 1.0 < [\text{Ti}] / 3.42[\text{N}] < 2.0$$

35 **[0021]** In formula 2, [Ti] and [N] represent the contents (wt%) of the corresponding elements)

[0022] In another exemplary embodiment of the present disclosure, the part includes, by volume fraction, 0.3-2% of a retained austenite structure and a residual tempered martensite structure.

[Advantageous Effects]

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[0023] A part with improved delayed fracture resistance for a high-strength a bolt according to an exemplary embodiment of the present disclosure improves formability during the processing of the thread part of a Mn-B steel bolt. Accordingly, delayed fracture in a 1 GPa-grade high-strength bolt may be suppressed by preventing cracks in the thread part of the bolt.

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[Brief Description of Drawings]

[0024] FIG. 1 is an image of a thread part of Comparative Example 3 before evaluation of delayed fracture resistance.

50 [Best Mode]

[0025] The present specification does not describe all elements of exemplary embodiments, and the description of general contents in the technical field to which the present disclosure belongs or contents overlapping between exemplary embodiments is omitted.

55 **[0026]** In addition, when a part is described to "include" a certain component, it means that it may further include other components rather than excluding other components, unless stated otherwise.

[0027] Singular expressions include plural expressions unless the context clearly indicates otherwise.

[0028] Hereinafter, the present disclosure is described in detail.

[0029] The following exemplary embodiments are provided to fully convey the idea of the present disclosure to those having ordinary knowledge in the technical field to which the present disclosure belongs. The present disclosure is not limited to the presented exemplary embodiments but may also be embodied in other forms.

[0030] The inventors of the present disclosure have found out that, by controlling the contents of Si and Mn, formability can be improved by optimizing the solid solution strengthening effect while ensuring strength and, thus, delayed fracture resistance can be improved as cracking caused by poor formability of a thread part is suppressed.

[0031] In addition, they have found out that a fine grain size can be obtained by controlling the contents of Ti and N and controlling the size of TiN inclusions and, through this, formability can be improved and delayed fracture resistance can be ensured.

[0032] A wire rod with improved delayed fracture resistance according to an exemplary embodiment of the present disclosure contains, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance.

[0033] The reason why the contents of the alloy elements are limited will be described in detail. The content is in wt% unit unless specified otherwise.

[0034] The content of carbon (C) is 0.15-0.30%.

[0035] C is an element added to ensure the strength of a product. If the carbon content is less than 0.15%, it is difficult to ensure the target strength. And, if it exceeds 0.30%, the delayed fracture characteristics may become inferior as the formation of retained austenite with superior mechanical stability is hindered by the hydrostatic pressure formed at the lath martensite during quenching. Therefore, in the present disclosure, the C content is limited to 0.15-0.30%.

[0036] The content of silicon (Si) is 0.15-0.25%.

[0037] Si is an element that is used not only for deoxidization of steel but also for ensuring strength through solid solution strengthening. If the Si content is less than 0.15%, the deoxidization of steel and improvement of strength through solid solution strengthening may be insufficient. And, if it exceeds 0.25%, formability and impact characteristics may become inferior due to solid solution strengthening. Therefore, in the present disclosure, the Si content is limited to 0.15-0.25%.

[0038] The content of manganese (Mn) is 0.95-1.35%.

[0039] Mn is an element which improves hardenability. It is a very useful element that provides solid solution strengthening effect by forming a substitutional solid solution in the matrix structure. If the Mn content is less than 0.95%, it is difficult to ensure the strength desired in the present disclosure because the solid solution strengthening effect and hardenability are insufficient. And, if the Mn content exceeds 1.35%, formability may become inferior due to the solid solution strengthening effect. Therefore, in the present disclosure, the Mn content is limited to 0.95-1.35%.

[0040] The content of phosphorus (P) is 0.030% or less (excluding 0%).

[0041] P is an element which is segregated in the grain boundary and lowers toughness and delayed fracture resistance. Therefore, in the present disclosure, the upper limit of the P content is limited to 0.030%.

[0042] The content of sulfur (S) is 0.030% or less (excluding 0%).

[0043] Like P, S is segregated in the grain boundary and lowers toughness. In addition, it hinders hot rolling by forming a low-melting-point emulsion. Therefore, in the present disclosure, the upper limit of the S content is limited to 0.030%.

[0044] The content of titanium (Ti) is 0.015-0.030%.

[0045] Ti is an element which binds to N introduced into steel to form titanium carbonitride (TiN). In the present disclosure, TiN can prevent cracking caused by poor formability of a part and improve delayed fracture resistance by reducing grain size. In addition, since Ti forms TiN, it can prevent free N from binding to B, which forms BN that worsens formability. If the Ti content is less than 0.015%, TiN is not formed enough and free N forms BN. As a result, the hardening effect of B cannot be utilized. And, if it exceeds 0.03%, delayed fracture resistance may become inferior due to formation of coarse carbonitride. Therefore, in the present disclosure, the Ti content is limited to 0.015-0.03%.

[0046] The content of boron (B) is 0.0010-0.0040%.

[0047] B is an element which improves hardenability. If the B content is less than 0.0010%, it is difficult to expect the improvement of hardenability. And, if it exceeds 0.0040%, the delayed fracture resistance becomes inferior since the austenite grain boundary becomes brittle as $\text{Fe}_{23}(\text{CB})_6$ carbide is formed in the grain boundary and the formability becomes inferior due to the formation of BN. Therefore, in the present disclosure, the B content is limited to 0.0010-0.0040%.

[0048] The content of nitrogen (N) is 0.0010-0.0080%.

[0049] N is an element that forms a carbonitride. If the N content is less than 0.0010%, the TiN precipitate that reduces grain size may not be formed enough. And, if it exceeds 0.0080%, the toughness and ductility of steel may become inferior due to the increased content of dissolved nitrogen and free N may bind with B to form BN which worsens formability. Therefore, in the present disclosure, the N content is limited to 0.0010-0.0080%.

[0050] The remaining component of the alloy composition is iron (Fe). But, the wire rod with improved delayed fracture resistance of the present disclosure may contain other impurities that can be included in common industrial steel production processes. These impurities are well known to those having ordinary knowledge in the art to which the present

disclosure belongs, and their types and contents are not specially limited in the present disclosure.

[0051] The wire rod with improved delayed fracture resistance according to an exemplary embodiment of the present disclosure satisfies formula 1:

$$\text{[Formula 1]} \quad 2.0 \leq 5.5 \times [\text{Si}] + [\text{Mn}] \leq 2.4$$

[0052] In formula 1, [Si] and [Mn] represent the contents (wt%) of the corresponding elements.

[0053] In the present disclosure, the contents of Si and Mn are controlled so that, while ensuring strength through the solid solution strengthening effect, the formability and delayed fracture resistance of a wire rod can be improved by suppressing excessive solid solution strengthening. The formula 1 is a formula for optimizing the solid solution strengthening effect. In the formula 1, if the value of $5.5 \times [\text{Si}] + [\text{Mn}]$ is smaller than 2.0, the strength desired by the present disclosure cannot be ensured. And, if the value of $5.5 \times [\text{Si}] + [\text{Mn}]$ exceeds 2.4, delayed fracture may be induced due to cracking caused by poor formability during the forming of a high-strength part owing to excessive solid solution strengthening. Therefore, in the present disclosure, the value of $5.5 \times [\text{Si}] + [\text{Mn}]$ is limited to 2.0-2.4 to improve the delayed fracture resistance.

[0054] In addition, the wire rod with improved delayed fracture resistance according to an exemplary embodiment of the present disclosure satisfies formula 2.

$$\text{[Formula 2]} \quad 1.0 < [\text{Ti}] / 3.42[\text{N}] < 2.0$$

[0055] In formula 2, [Ti] and [N] represent the contents (wt%) of the corresponding elements.

[0056] The present disclosure aims at improving the delayed fracture resistance of a wire rod by reducing grain size and improving formability. The inventors of the present disclosure have found out that grain size can be reduced by controlling the size of TiN inclusions and formability and delayed fracture resistance can be ensured by suppressing the formation of BN. The formula 2 is a formula derived to control the size of TiN inclusions and suppress the formation of BN. In the formula 2, if the value of $[\text{Ti}] / 3.42[\text{N}]$ is 1.0 or smaller, formability may become inferior due to BN, etc. formed by free N not bound to Ti. And, if the value of $[\text{Ti}] / 3.42[\text{N}]$ is 2.0 or larger, the size of TiN inclusions is increased due to excess Ti and the grain refinement effect cannot be achieved. Therefore, in the present disclosure, the value of $[\text{Ti}] / 3.42[\text{N}]$ is limited to satisfy $1.0 < [\text{Ti}] / 3.42[\text{N}] < 2.0$.

[0057] In the present disclosure, the size of TiN inclusions for reducing grain size may be 15 μm or smaller. If the size of the TiN inclusions exceeds 15 μm , it is difficult to ensure delayed fracture resistance through grain refinement.

[0058] A part with improved delayed fracture resistance manufactured from the wire rod according to the present disclosure includes, by volume fraction, 0.3-2% of a retained austenite structure and a residual tempered martensite structure. If the fraction of the retained austenite structure is less than 0.3%, it is difficult to expect the role as a barrier that delays the diffusion of hydrogen. And, if it exceeds 2%, the retained austenite is formed thickly not only in the lath boundary but also in the austenite grain boundary, etc., which makes it difficult to delay the diffusion of hydrogen and lowers the effect of improving delayed fracture resistance.

[0059] Next, a method for manufacturing a wire rod and a part with improved delayed fracture resistance according to an exemplary embodiment of the present disclosure will be described.

[0060] The wire rod and a part with improved delayed fracture resistance according to the present disclosure may be manufactured by various methods without particular limitation. As an exemplary embodiment, it may be manufactured by the following method.

[0061] The wire rod with improved delayed fracture resistance according to the present disclosure may be manufactured by a method including: a step of finish-rolling a steel material containing, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance at 880-980 °C; and step of winding at 830-930 °C.

[0062] First, a steel material satisfying the above alloy composition is prepared and finish-rolled at 880-980 °C into a wire rod. Then, the rolled wire rod is wound at 830-930 °C into a coil shape.

[0063] If the wire rod rolling temperature is below 880 °C or if the winding temperature is below 830 °C, a decarburized ferrite layer may be formed on the surface through phase transformation because the surface layer is a quasi-two-phase, and the delayed fracture resistance may become inferior since a decarburized ferrite layer is formed also on the surface of the bolt during heat treatment. In addition, delayed fracture resistance may become inferior since the prior austenite grain size of the bolt decreases and the fraction of retained austenite increases. If the wire rod finish rolling temperature exceeds 980 °C or if the winding temperature exceeds 930 °C, a decarburized ferrite layer may be formed on the surface as decarburization is accelerated by hydrogen and the delayed fracture resistance may become inferior as the prior austenite grain size is increased.

[0064] Then, the wound wire rod may be drawn, spheroidization heat-treated, coated, formed into a bolt, austenitized, quenched and then tempered to obtain a final part for a bolt. For example, it may be prepared by the following method.

[0065] A method for manufacturing a part for a bolt according to an exemplary embodiment of the present disclosure includes: a step of drawing the wire rod manufactured according to the present disclosure; a step of spheroidization heat-treating the drawn wire rod at 745-770 °C; a step of heating the spheroidization heat-treated drawn wire rod at 870-940 °C; a step of quenching the spheroidization heat-treated drawn wire rod at 50-80 °C; and a step of tempering at 400-600 °C.

[0066] The spheroidization heat treatment may be performed at 745-770 °C. If the heat treatment temperature is below 745 °C or exceeds 770 °C, the degree of spheroidization may be decreased, which may cause increased hardness, poor formability of a thread part of the bolt after forming, and cracking of the thread part.

[0067] The austenitization heat treatment may be performed at 870-940 °C. If the heat treatment temperature is below 870 °C, toughness may become inferior as a martensite structure is formed nonuniformly after quenching due to insufficient reverse austenite transformation. If the heat treatment temperature exceeds 940 °C, delayed fracture resistance may become inferior due to increased prior austenite grain size.

[0068] The quenching may be performed at 50-80 °C. If the quenching temperature is below 50 °C, fine quenching cracks may occur in the thread of the bolt due to thermal deformation, which can cause delayed fracture. And, if it exceeds 80 °C, retained austenite may be formed in the prior austenite grain boundary in addition to the mechanically stable retained austenite formed in the lath due to insufficient quenching, and delayed fracture may be induced due to accumulation of hydrogen.

[0069] The tempering may be performed at 400-600 °C in order to provide strength and toughness according to the use and purpose of the final product. If the tempering temperature is below 400 °C, brittleness may be caused by the tempering. And, if it exceeds 600 °C, it is difficult to achieve the strength desired by the present disclosure.

[0070] The part with improved delayed fracture resistance manufactured according to the present disclosure includes, by volume fraction, 0.3-2% of a retained austenite structure and a residual tempered martensite structure.

[0071] Hereinafter, the present disclosure is described in more detail through examples. However, the following examples merely illustrate the present disclosure and the present disclosure is not limited by the examples. The scope of the present disclosure is determined by the appended claims and the matters reasonably inferred therefrom.

Examples

[0072] Wire rods of Examples 1-9 and Comparative Examples 1-7 satisfying the alloy composition of Table 1 were prepared into final bolts for test under to the manufacturing condition of the present disclosure. Specifically, a steel piece satisfying the alloy composition of Table 1 was finish-rolled at 880-980 °C into a wire rod and wound into a coil shape at 830-930 °C. The wound wire rod was spheroidization heat-treated at 745-770 °C. Then, the spheroidization heat-treated wire rod was formed into a bolt, austenitized at 870-940 °C, quenching at 50-80 °C, and then tempered at 400-600 °C to ensure a tensile strength of 1050 ± 16 MPa.

[Table 1]

	Alloy composition (wt%)							
	C	Si	Mn	P	S	Ti	B	N
Ex. 1	0.29	0.21	0.99	0.011	0.005	0.018	0.0023	0.0041
Ex. 2	0.16	0.20	1.30	0.012	0.005	0.019	0.0020	0.0049
Ex. 3	0.24	0.19	0.96	0.008	0.005	0.027	0.0024	0.0040
Ex. 4	0.21	0.20	1.11	0.010	0.005	0.018	0.0023	0.0051
Ex. 5	0.23	0.16	1.20	0.009	0.005	0.028	0.0020	0.0048
Ex. 6	0.22	0.23	0.99	0.010	0.005	0.025	0.0019	0.0055
Comp. Ex. 1	0.23	0.19	0.98	0.008	0.005	0.018	0.0023	0.0021
Comp. Ex. 2	0.24	0.21	1.02	0.010	0.005	0.042	0.0021	0.0040
Comp. Ex. 3	0.20	0.26	1.15	0.009	0.005	0.019	0.0020	0.0050
Comp. Ex. 4	0.23	0.21	1.45	0.011	0.005	0.022	0.0021	0.0050
Comp. Ex. 5	0.33	0.20	1.10	0.010	0.005	0.018	0.0022	0.0050

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[0073] After evaluating the maximum size of TiN precipitate and delayed fracture cracks for the bolts of Examples 1-6 and Comparative Examples 1-5, the values of the formula 1 and formula 2 were determined. The result is given in Table 2. The maximum size of TiN precipitate was defined by the maximum size of inclusions observed in the L-section (longitudinal direction) of the bolt in an area of 160 mm² for 30 fields by extreme value analysis. The result is also given Table 2.

[0074] The delayed fracture resistance was tested according to the delayed fracture simulation method by fastening the bolt with a clamping force corresponding to the yield strength and immersing in a solution of 5% hydrochloric acid + 95% distilled water for 10 minutes. The presence of cracks in the thread, which is the part where stress is concentrated, was observed. X indicates no cracking, and O indicates the occurrence of cracks.

[Table 2]

	Formula 1 $5.5 \times [\text{Si}] + [\text{Mn}]$	Formula 2 $[\text{Ti}] / 3.42[\text{N}]$	Maximum TiN size (μm)	Presence of delayed fracture cracks
Ex. 1	2.15	1.284	13.2	X
Ex. 2	2.40	1.134	11.1	X
Ex. 3	2.01	1.974	14.5	X
Ex. 4	2.21	1.032	10.2	X
Ex. 5	2.08	1.706	13.9	X
Ex. 6	2.26	1.329	12.1	X
Comp. Ex. 1	2.03	2.506	15.9	O
Comp. Ex. 2	2.18	3.070	17.8	O
Comp. Ex. 3	2.58	1.111	10.3	O
Comp. Ex. 4	2.61	1.287	13.5	O
Comp. Ex. 5	2.20	1.053	11.5	O

[0075] As seen from Table 2, for Examples 1-6, wherein the requirements of alloy composition, formulas and TiN size proposed by the present disclosure are satisfied, showed no delayed fracture crack in the thread part of the bolt before and after the evaluation of delayed fracture resistance. In contrast, for Comparative Example 1, wherein the $[\text{Ti}] / 3.42[\text{N}]$ value exceeds the upper limit 2.0 proposed by the present disclosure as 2.506, coarse TiN was formed and delayed fracture cracks occurred.

[0076] For Comparative Example 2, wherein the $[\text{Ti}] / 3.42[\text{N}]$ value exceeds the upper limit 2.0 proposed by the present disclosure as 3.070, coarse TiN was formed and delayed fracture cracks occurred.

[0077] For Comparative Example 3, wherein the Si content exceeds the upper limit 0.25% proposed by the present disclosure as 0.26% and the $5.5 \times [\text{Si}] + [\text{Mn}]$ value exceeds the upper limit 2.4 as 2.58, delayed fracture cracks occurred due to poor formability of the bolt thread part after the spheroidization heat treatment because of excessive solid solution strengthening. FIG. 1 shows the image of the thread part for Comparative Example 3 before the evaluation of delayed fracture resistance. As seen from FIG. 1, delayed fracture cracks occurred for Comparative Example 3, which does not satisfy the requirements proposed by the present disclosure, indicating that delayed fracture resistance was not achieved.

[0078] For Comparative Example 4, wherein the Mn content exceeds the upper limit 1.35% proposed by the present disclosure as 1.45% and the $5.5 \times [\text{Si}] + [\text{Mn}]$ value exceeds the upper limit 2.4 proposed by the present disclosure as 2.61, delayed fracture cracks occurred due to poor formability of the bolt thread part after the spheroidization heat treatment because of excessive solid solution strengthening.

[0079] For Comparative Example 5, wherein the C content exceeds the upper limit 0.30% proposed by the present disclosure as 0.33%, the formation of a retained austenite structure with superior mechanical stability was prevented and delayed fracture cracks occurred.

[0080] In addition, final bolt samples of Example 3 and Comparative Examples 6-1 to 6-6 were prepared under to the conditions described in Table 3.

[Table 3]

	Temperature (°C)				Presence of delayed fracture cracks	
	Finish rolling temperature	Winding temperature	Spheroidization heat treatment temperature	Austenitization temperature		
5	Ex. 3	930	880	755	910	X
10	Comp. Ex. 6-1	990	940	755	910	O
	Comp. Ex. 6-2	870	820	755	910	O
15	Comp. Ex. 6-3	930	880	755	950	O
	Comp. Ex. 6-4	930	880	755	860	O
20	Comp. Ex. 6-5	930	880	740	910	O
	Comp. Ex. 6-6	930	880	775	910	O

[0081] For Example 3, wherein the finish rolling temperature, winding temperature, spheroidization heat treatment temperature and austenitization temperature are satisfied, delayed fracture crack did not occur. In contrast, for Comparative Example 6-1, wherein the rolling temperature exceeds the upper limit 980 °C proposed by the present disclosure as 990 °C and the winding temperature also exceeds the upper limit 930 °C proposed by the present disclosure as 940 °C, delayed fracture cracks occurred as the prior austenite grain size was increased in the wire rod and in the bolt as well.

[0082] For Comparative Example 6-2, wherein the rolling temperature does not reach the lower limit 880 °C proposed by the present disclosure as 870 °C and the winding temperature also does not reach the lower limit 830 °C proposed by the present disclosure as 820 °C, the fraction of retained austenite was increased and delayed fracture crack occurred as the prior austenite grain size was increased in the wire rod and in the bolt as well.

[0083] For Comparative Example 6-3, wherein the austenitization heat treatment temperature exceeds the upper limit 940 °C proposed by the present disclosure as 950 °C, delayed fracture cracks occurred as the prior austenite grain size of the bolt was increased.

[0084] For Comparative Example 6-4, wherein the austenitization heat treatment temperature does not reach the lower limit 870 °C proposed by the present disclosure as 860 °C, undissolved ferrite was formed because the QT heat treatment was conducted in the state where the bolt was not austenitized enough and, accordingly, delayed fracture cracks occurred.

[0085] For Comparative Example 6-5, wherein the spheroidization temperature does not reach the lower limit 745 °C proposed by the present disclosure as 740 °C, and for Comparative Example 6-6, wherein the spheroidization temperature exceeds the upper limit 770 °C proposed by the present disclosure as 775 °C, formability was inferior and delayed fracture cracks occurred due to low degree of spheroidization.

[0086] Although the exemplary embodiments of the present disclosure were described, the present disclosure is not limited thereto and those having ordinary knowledge in the art will understand that various changes and modifications without departing from the concept and scope of the appended claims.

Claims

1. A wire rod with improved delayed fracture resistance, comprising, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance, and satisfying formula 1:

$$[\text{Formula 1}] \quad 2.0 \leq 5.5 \times [\text{Si}] + [\text{Mn}] \leq 2.4$$

wherein [Si] and [Mn] represent the contents (wt%) of the corresponding elements.

2. The wire rod according to claim 1, which satisfies formula 2:

$$[\text{Formula 2}] \quad 1.0 < [\text{Ti}] / 3.42[\text{N}] < 2.0$$

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wherein [Ti] and [N] represent the contents (wt%) of the corresponding elements.

3. The wire rod according to claim 1, wherein the size of TiN inclusions is 15 μm or smaller.

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4. A method for manufacturing a wire rod with improved delayed fracture resistance, comprising:

a step of finish-rolling a steel material comprising, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance and satisfying formula 1 at 880-980 °C; and a step of winding at 830-930 °C.

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$$[\text{Formula 1}] \quad 2.0 \leq 5.5 \times [\text{Si}] + [\text{Mn}] \leq 2.4$$

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wherein [Si] and [Mn] represent the contents (wt%) of the corresponding elements.

5. The method for manufacturing a wire rod according to claim 4, wherein the steel material satisfies formula 2:

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$$[\text{Formula 2}] \quad 1.0 < [\text{Ti}] / 3.42[\text{N}] < 2.0$$

wherein [Ti] and [N] represent the contents (wt%) of the corresponding elements.

6. A method for manufacturing a part with improved delayed fracture resistance, comprising:

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a step of drawing a wire rod manufactured according to claim 4 or 5;
a step of spheroidization heat-treating the drawn wire rod at 745-770 °C;
a step of heating the spheroidization heat-treated drawn wire rod at 870-940 °C;
a step of quenching the spheroidization heat-treated drawn wire rod at 50-80 °C; and
a step of tempering the quenched part at 400-600 °C.

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7. A part with improved delayed fracture resistance, comprising, by wt%, 0.15-0.30% of C, 0.15-0.25% of Si, 0.95-1.35% of Mn, 0.030% or less of P, 0.030% or less of S, 0.015-0.030% of Ti, 0.0010-0.0040% of B, 0.0010-0.0080% of N, and Fe and inevitable impurities as the balance, and satisfying formula 1:

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$$[\text{Formula 1}] \quad 2.0 \leq 5.5 \times [\text{Si}] + [\text{Mn}] \leq 2.4$$

wherein [Si] and [Mn] represent the contents (wt%) of the corresponding elements.

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8. The part according to claim 7, which satisfies formula 2:

$$[\text{Formula 2}] \quad 1.0 < [\text{Ti}] / 3.42[\text{N}] < 2.0$$

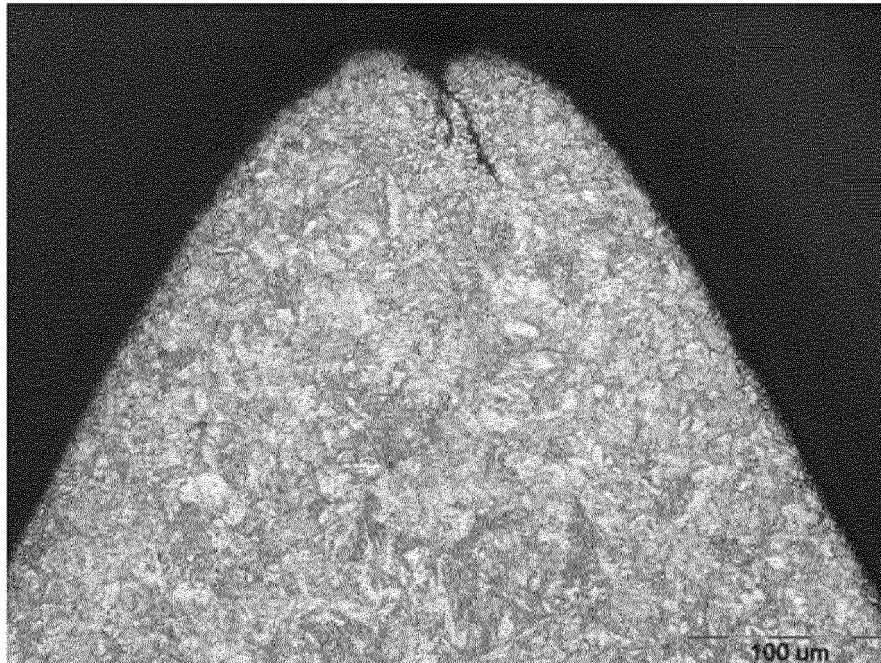
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wherein [Ti] and [N] represent the contents (wt%) of the corresponding elements.

9. The part according to claim 7, which comprises, by volume fraction, 0.3-2% of a retained austenite structure and a residual tempered martensite structure.

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【FIG. 1】



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2021/018977

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A. CLASSIFICATION OF SUBJECT MATTER		
C22C 38/00(2006.01)i; C22C 38/02(2006.01)i; C22C 38/04(2006.01)i; C22C 38/14(2006.01)i; C21D 9/52(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(2006.01); C21D 8/02(2006.01); C21D 8/06(2006.01); C22C 38/02(2006.01); C22C 38/04(2006.01); C22C 38/14(2006.01)		
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: 규소(silicon), 망간(manganese), 티타늄(titanium), 붕소(boron), 가열(heating), 선재(wire rod), 강선(steel wire), 볼트(bolt), 템퍼링(tempering)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2012-0099153 A (NIPPON STEEL CORPORATION) 06 September 2012 (2012-09-06) See paragraph [0081], claims 1-3 and table 3.	1-5,7-9
Y		6
Y	KR 10-2010-0076743 A (POSCO) 06 July 2010 (2010-07-06) See paragraphs [0054]-[0058] and claim 7.	6
A	JP 2013-234349 A (NIPPON STEEL & SUMITOMO METAL CORP.) 21 November 2013 (2013-11-21) See paragraph [0046] and claims 1-2.	1-9
A	KR 10-2007-0086836 A (NIPPON STEEL CORPORATION) 27 August 2007 (2007-08-27) See paragraph [0118] and claims 1-4.	1-9
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" 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 "D" document cited by the applicant in the international application "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 "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 "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 05 April 2022		Date of mailing of the international search report 06 April 2022
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208 Facsimile No. +82-42-481-8578		Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
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C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 107815594 A (HUNAN HUALING XIANGTAN IRON & STEEL CO., LTD.) 20 March 2018 (2018-03-20) See claim 1.	1-9

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. PCT/KR2021/018977

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Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
KR 10-2012-0099153 A	06 September 2012	CN 102741441 A	17 October 2012
		CN 102741441 B	11 September 2013
		JP 5026626 B2	12 September 2012
		JP WO2011-108459 A1	27 June 2013
		KR 10-1297539 B1	14 August 2013
		WO 2011-108459 A1	09 September 2011
KR 10-2010-0076743 A	06 July 2010	KR 10-1091446 B1	07 December 2011
JP 2013-234349 A	21 November 2013	JP 5776623 B2	09 September 2015
KR 10-2007-0086836 A	27 August 2007	CN 101098979 A	02 January 2008
		JP 2006-225701 A	31 August 2006
		JP 2006-316291 A	24 November 2006
		JP 4669300 B2	13 April 2011
		JP 4669317 B2	13 April 2011
		KR 10-1033752 B1	09 May 2011
		TW 200641144 A	01 December 2006
		TW I318645 B	21 December 2009
		WO 2006-088019 A1	24 August 2006
CN 107815594 A	20 March 2018	None	