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(54) **WIRE ROD AND STEEL WIRE USING SAME**

(57) A wire rod contains C, Si, Mn, N, Al, P, and S in predetermined contents with the remainder being iron and inevitable impurities. The Al and N contents meet a condition specified by Expression (1) as follows: $[Al] \leq 2.1 \times 10 \times [N] + 0.255$ (1), where [Al] and [N] are contents (in mass percent) of Al and N, respectively. The wire rod has a microstructure including 95 percent by area or more of a pearlite. The wire rod has an AlN content of 0.005% or more and a percentage of AlN particles having a diameter d_{GM} of 10 to 20 μm of 50% or more (in number

percent) in an extreme value distribution of maximum values of the diameters d_{GM} of AlN particles, where the d_{GM} refers to a geometrical mean $(ab)^{1/2}$ of a length "a" and a thickness "b" of an AlN particle. The wire rod is usable typically for a high-strength prestressing steel wire and wire rope that less suffer from reduction in delayed fracture resistance with an increasing strength and have delayed fracture resistance conforming building standards.

EP 2 832 878 A1

Description

Technical Field

5 **[0001]** The present invention relates to a wire rod and a steel wire using the same each of which is used for or as prestressing steel wires and wire ropes.

Background Art

10 **[0002]** There are strong demands for concrete members to have a higher strength and a lighter weight in civil engineering and construction areas. Prestressed concrete (hereinafter also referred to as "PC") is well known as a way to strengthen such concrete members. In the prestressed concrete, compression stress is applied to material concrete by using steel wires. Such a steel wire for PC, namely, a prestressing steel wire (PC steel wire), when having a higher strength, can contribute more satisfactorily to a higher strength and a lighter weight of PC. There is now known a
15 prestressing strand including 7 wires with a diameter of 15.2 mm and having a maximum force of about 261 kN, as prescribed in Japanese Industrial Standard (JIS) G3536.

[0003] In addition to Japanese Industrial Standards, various standards (specifications) and recommended tests are prescribed for prestressing steel wires from the viewpoint of architectural safety. In particular, it is important to take delayed fracture resistance into consideration when a high strength prestressing steel wire is applied. The delayed
20 fracture is a phenomenon where, when a steel is used for a long time under the application of a stress, hydrogen migrated into the steel accumulates typically in a fine flaw in the steel surface, causes a microstructure around the flaw to become brittle, and thereby induces brittle fracture. The prestressing steel wires are used while being always tensed and may possibly undergo delayed fracture. To prevent this, strict specifications are prescribed on them. In particular, the prestressing steel wires are well known to become more susceptible to delayed fracture with an increasing strength. Demands
25 are therefore made to develop steels that can less suffer from delayed fracture even when having a higher strength.

[0004] Typically, Patent Literature 1 discloses a technique of improving delayed fracture resistance of a prestressing steel wire having a carbon content of 0.6% to 1.1%. According to the technique, a wire rod after wire drawing is subjected to blueing at a temperature of 450°C or higher to spheroidize plate-like cementite to thereby improve the delayed fracture resistance. The technique in Patent Literature 1, however, causes the steel wire to have a low strength due to the
30 spheroidization of plate-like cementite, thereby has limitations in strength improvement, and disadvantageously fails to help the steel wire to have a wire strength of 2000 MPa or more.

[0005] Patent Literature 2 discloses a technique of improving delayed fracture resistance of a prestressing steel wire having a carbon content of 0.6% to 1.3%. The improvement is achieved by imparting a compressive residual stress to a surface layer of the steel wire and thereby forming a deformed pearlite in the surface layer. The technique in Patent
35 Literature 2, however, is applied to prestressing steel wires having a wire strength of up to about 1600 MPa and may probably fail to sufficiently ensure resistance to delayed fracture that is caused by hydrogen diffusion at higher wire strengths of typically 2000 MPa or more.

[0006] Patent Literature 3 discloses a technique of improving delayed fracture resistance in a tempered martensite phase of not a prestressing steel wire, but a bearing steel having a carbon content of 0.65% to 1.20%. The improvement
40 is achieved by dispersing particles typically of Ti- or Al-containing nitrides having a particle size of 50 to 300 nm in an amount at a predetermined or higher so as to trap hydrogen. However, hydrogen behaves differently in different microstructures, and dimensions, amounts, and other factors of precipitates acting as appropriate trapping sites also differ in different microstructures. This impedes the application of the technique in Patent Literature 3 typically to a prestressing steel wire without modification, where the prestressing steel wire includes a pearlite as a main phase. A manufacturing
45 process for such a bearing steel performs a quenching-tempering treatment after wire drawing; whereas a manufacturing process for a prestressing steel wire performs wire drawing after a patenting treatment. Thus, the two manufacturing processes significantly differ from each other and employ different procedures to control precipitation typically of nitrides.

Citation List

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Patent Literature

[0007]

55 Patent Literature 1: Japanese Unexamined Patent Application Publication (JP-A) No. 2004-360005
Patent Literature 2: JP-A No. 2004-131797
Patent Literature 3: Japanese Patent No. 3591236

Summary of Invention

Technical Problem

[0008] An object of the present invention is to provide a wire rod including a pearlite as a main phase, where the wire rod less suffers from reduction in delayed fracture resistance even when having a high strength and is usable typically as a high strength prestressing steel wire and wire rope that have such delayed fracture resistance as to meet building standards.

Solution to Problem

[0009] The present inventors made investigations on inclusions having a hydrogen trap effect in a wire rod including a pearlite as a main phase. As a result, they have found that it is important to ensure AlN particles in an amount at a predetermined level or higher and to ensure, of such AlN particles, AlN particles having a size of 10 to 20 μm in an amount at a predetermined level or higher. Specifically, the present invention provides, in an aspect, a wire rod including C in a content of 0.8% to 1.2% (in mass percent, hereinafter the same for chemical composition); Si in a content of 0.1% to 2.0%; Mn in a content of 0.1% to 2.0%; N in a content of 0.002% to 0.010%; Al in a content of 0.04% to 0.15%; P in a content of 0.02% or less (including 0%); and S in a content of 0.02% or less (including 0%), with the remainder being iron and inevitable impurities, in which the Al content and N content meet a condition specified by Expression (1) given as follows:

$$[\text{Al}] \leq -2.1 \times 10 \times [\text{N}] + 0.255 \quad (1)$$

where $[\text{Al}]$ and $[\text{N}]$ are contents (in mass percent) of Al and N, respectively; the wire rod has a microstructure including 95 percent by area or more of a pearlite; the wire rod has a content of AlN of 0.005% or more; and a percentage of AlN particles having a diameter d_{GM} of 10 to 20 μm is 50% or more in number percent in an extreme value distribution of maximum values of the diameters d_{GM} of AlN particles, where the diameter d_{GM} is represented by a geometrical mean $(ab)^{1/2}$ of a length "a" and a thickness "b" of an AlN particle. In a preferred embodiment, the wire rod may have a solute nitrogen content of 0.003% or less.

[0010] According to preferred embodiments of the present invention, the wire rod may further contain any of (a) at least one element selected from the group consisting of Cr in a content of 1.0% or less (excluding 0%), Ni in a content of 1.0% or less (excluding 0%), Co in a content of 1.0% or less (excluding 0%), Mo in a content of 1.0% or less (excluding 0%), and Cu in a content of 0.5% or less (excluding 0%); and (b) at least one element selected from the group consisting of B in a content of 0.005% or less (excluding 0%), Nb in a content of 0.5% or less (excluding 0%), and V in a content of 0.5% or less (excluding 0%).

[0011] The present invention also includes a steel wire obtained from the wire rod. Advantageous Effects of Invention

[0012] The present invention adjusts the Al and N contents appropriately and controls the total content of AlN particles and the content of AlN particles having a predetermined size (d_{GM} of 10 to 20 μm) appropriately. The present invention can therefore provide a wire rod having excellent delayed fracture resistance. The present invention, in the preferred embodiment, adjusts a solute nitrogen content at a predetermined level or higher and can thereby help the steel wire to have better twisting properties.

Description of Embodiments

[0013] After intensive investigations, the present inventors have found that, in a wire rod including a pearlite as a main phase, it is effective to ensure AlN (particles) in a predetermined content as a hydrogen trap site and to ensure AlN particles having a size of 10 to 20 μm in a content at a predetermined level or higher.

[0014] The AlN content is specified to 0.005% or more, because the wire rod offers an increasing hydrogen trap effect with an increasing AlN content. The AlN content is preferably 0.006% or more, more preferably 0.007% or more, and particularly preferably 0.01% or more. Though not critical, the upper limit of the AlN content is generally about 0.04%.

[0015] A extreme value distribution of maximum values is herein employed as an index for ensuring AlN particles having a size of 10 to 20 μm in a number at a predetermined level or higher. Initially, a geometrical mean $(ab)^{1/2}$ of the length "a" and the thickness "b" of an AlN particle is employed as a size of the AlN particle and is indicated as d_{GM} (μm). As used herein the term "length "a"" of an AlN particle refers to the length (dimension) of the AlN particle in the wire rod longitudinal direction; and the term "thickness "b"" of the AlN particle refers to a dimension of the AlN particle in a direction perpendicular to the wire rod longitudinal direction.

[0016] The term "extreme value distribution of maximum values of d_{GM} " refers to a distribution determined by measuring a maximum d_{GM} (max) among d_{GM} values of AlN particles present in a predetermined area; repeating this procedure on two or more view fields; and subjecting the measured two or more d_{GM} (max) values to a statistical processing. The percentage of AlN particles having a d_{GM} (max) of 10 to 20 μm is 50% or more (in number percent) in the extreme value distribution in the embodiment of the present invention. If AlN particles having a size d_{GM} greater than 20 μm is present in a large number percent, AlN particles are present in a smaller total number and may fail to exhibit the hydrogen trap effect sufficiently. In addition, such AlN particles having a size d_{GM} less than 10 μm exhibit a lower hydrogen trap effect. AlN particles that are effective for hydrogen trap can therefore be ensured sufficiently by controlling AlN particles having a d_{GM} (max) of 10 to 20 μm to be present in a number percent of 50% or more in the extreme value distribution.

[0017] The wire rod according to the embodiment of the present invention includes a pearlite that occupies 95 percent by area or more of the main phase. The area percentage of the pearlite is preferably 97% or more, and more preferably 100%.

[0018] Next, chemical compositions of the wire rod according to the embodiment of the present invention will be illustrated below.

Carbon (C) content: 0.8% to 1.2%

[0019] Carbon (C) element effectively contributes to a higher strength. The wire rod and a steel wire after cold working have higher strengths with an increasing carbon content. The carbon content is therefore specified to 0.8% or more. The carbon content is preferably 0.85% or more, and more preferably 0.90% or more. However, carbon, if present in an excessively high content, may cause aging embrittlement during cold wire drawing, thereby cause the steel wire to have inferior toughness, and disadvantageously invite cracking during stranding. To prevent this, the carbon content is specified to 1.2% or less. The carbon content is preferably 1.1% or less, and more preferably 1.05% or less.

Silicon (Si) content: 0.1% to 2.0%

[0020] Silicon (Si) element not only acts as a deoxidizer, but also effectively has actions of helping the wire rod to have a higher strength and to offer better relaxation properties. When hot dip galvanizing is applied to the wire rod, silicon element also offers an action of suppressing strength reduction occurring upon galvanizing. To exhibit these actions effectively, the Si content is specified to 0.1% or more. The Si content is preferably 0.2% or more, and more preferably 0.4% or more. In contrast, Si, if present in an excessively high content, may cause the wire rod to have inferior cold wire drawability and to suffer from a higher breakage ratio. To prevent this, the Si content is specified to 2.0% or less. The Si content is preferably 1.8% or less, and more preferably 1.5% or less.

Manganese (Mn) content: 0.1% to 2.0%

[0021] Manganese (Mn) element not only act as a deoxidizer as with Si, but also particularly has an action of fixing sulfur (S) in the steel as MnS and helping the steel to have better toughness and ductility. To exhibit these actions effectively, the Mn content is specified to 0.1% or more. The Mn content is preferably 0.15% or more, and more preferably 0.2% or more. However, manganese element is readily segregated and, if added in excess, may cause the formation of supercooled phases such as martensite because of excessively increased hardenability of a region where Mn is segregated. To prevent this, the Mn content is specified to 2.0% or less. The Mn content is preferably 1.8% or less, and more preferably 1.5% or less.

Nitrogen (N) content: 0.002% to 0.010%

[0022] Nitrogen (N) element is important for the formation of AlN that features the embodiment of the present invention and is contained in a content of 0.002% or more. The nitrogen content is preferably 0.0025% or more, more preferably 0.0030% or more, and particularly preferably 0.0040% or more. However, nitrogen, if added in excess, may cause the wire rod to have inferior twisting properties due to an increased solute nitrogen content. This is because nitrogen dissolves as an interstitial element in the steel as with carbon and causes embrittlement due to strain aging. To prevent this, the nitrogen content is specified to 0.010% or less. The nitrogen content is preferably 0.0090% or less, and more preferably 0.0080% or less.

Solute nitrogen content: 0.003% or less

[0023] Solute nitrogen causes inferior twisting properties and is preferably minimized in amount. The solute nitrogen content is therefore preferably 0.003% or less, more preferably 0.002% or less, and furthermore preferably 0.001% or

less. The solute nitrogen content may be controlled typically by adjusting the contents of nitride-forming elements such as Al, B, and Nb; and the nitrogen content.

Aluminum (Al) content: 0.04% to 0.15% and $[Al] \leq -2.1 \times 10 \times [N] + 0.255$

[0024] Aluminum (Al) element acts as a deoxidizer and is important herein, because aluminum is combined with nitrogen to form AlN, thereby traps hydrogen, and helps the wire rod to have better delayed fracture resistance. The aluminum nitride AlN also effectively contributes to grain refinement by a pinning effect. To exhibit these effects effectively, the Al content is specified to 0.04% or more. The Al content is preferably 0.05% or more, and more preferably 0.055% or more. In contrast, Al, if present in an excessively high content particularly in a range of high nitrogen contents, may form coarse AlN particles, and this may reduce the hydrogen trap effect of AlN. To prevent this, the Al content is specified to 0.15% in terms of its upper limit and is adapted to meet a condition specified by Expression (1) given as follows.

[0025] [Math.1]

$$[Al] \leq -2.1 \times 10 \times [N] + 0.255 \quad (1)$$

[0026] In Expression (1), [Al] and [N] denote contents (in mass percent) of Al and N, respectively. Expression (1) is an expression that has been derived from many experimental examples in which delayed fracture resistance was examined at varying nitrogen contents and aluminum contents. When the Al content meets the condition specified by Expression (1), the upper limit of the Al content is more strictly controlled in a range of high nitrogen contents so as to suppress the formation of coarse AlN particles. The Al content is preferably 0.14% or less, and more preferably 0.12% or less in terms of its upper limit.

Phosphorus (P) content: 0.02% or less (including 0%)

[0027] Phosphorus (P) element is segregated at a prior austenite grain boundary, makes the grain boundary brittle, and causes the wire rod to have inferior fatigue properties. To prevent this, the phosphorus content is preferably minimized and is specified herein to 0.02% or less. The phosphorus content is preferably 0.015% or less, and more preferably 0.010% or less.

Sulfur (S) content: 0.02% or less (including 0%)

[0028] Sulfur (S) element is segregated at a prior austenite grain boundary, makes the grain boundary brittle, and causes the wire rod to have inferior fatigue properties, as with phosphorus. To prevent this, the sulfur content is preferably minimized and is herein specified to 0.02% or less. The sulfur content is preferably 0.015% or less, and more preferably 0.010% or less.

[0029] The wire rod according to the embodiment of the present invention has a basic chemical composition as above, with the remainder substantially being iron. However, inevitable impurities are naturally acceptable, where the inevitable impurities are brought into the steel under conditions typically of raw materials, facility materials, and manufacturing facilities and are contained in the steel. According to necessity to have further better properties such as strength, toughness, and ductility, the wire rod according to the embodiment of the present invention may further contain any of elements as follows.

[0030] At least one element selected from the group consisting of Cr in a content of 1.0% or less (excluding 0%), Ni in a content of 1.0% or less (excluding 0%), Co in a content of 1.0% or less (excluding 0%), Mo in a content of 1.0% or less (excluding 0%), and Cu in a content of 0.5% or less (excluding 0%)

[0031] Chromium (Cr) element has actions of reducing lamellar spacing of pearlite and helping the wire rod to have a higher strength and better toughness. To exhibit these actions effectively, the Cr content is preferably 0.05% or more, more preferably 0.1% or more, and furthermore preferably 0.2% or more. In contrast, Cr, if present in an excessively high content, may cause the wire rod to have higher hardenability and thereby increase the risk of the formation of a supercooled phase during hot rolling. To prevent this, the Cr content is preferably 1.0% or less, more preferably 0.6% or less, and furthermore preferably 0.5% or less.

[0032] Nickel (Ni) element helps the steel wire after wire drawing to have better toughness. To exhibit such actions effectively, the Ni content is preferably 0.05% or more, more preferably 0.1% or more, and furthermore preferably 0.2% or more. However, Ni, if added in excess, may exhibit saturated effects, thus being economically useless. To prevent this, the Ni content is preferably 1.0% or less, more preferably 0.7% or less, and furthermore preferably 0.6% or less.

[0033] Cobalt (Co) element has actions of reducing pro-eutectoid cementite (particularly at a high carbon content) and

helping the wire rod to more readily control its microstructure to be a homogeneous pearlite. To exhibit these actions effectively, the Co content is preferably 0.05% or more, more preferably 0.1% or more, and furthermore preferably 0.2% or more. However, Co, if added in excess, may exhibit saturated effects, thus being economically useless. To prevent this, the Co content is preferably 1.0% or less, more preferably 0.8% or less, and furthermore preferably 0.6% or less.

[0034] Molybdenum (Mo) element helps the steel wire to have better corrosion resistance. To exhibit such actions effectively, the Mo content is preferably 0.05% or more, and more preferably 0.1% or more. However, Mo, if present in an excessively high content, may cause the formation of a supercooled phase more readily during hot rolling and cause the wire rod to have inferior ductility. To prevent this, the Mo content is preferably 1.0% or less, more preferably 0.5% or less, and furthermore preferably 0.3% or less.

[0035] Copper (Cu) element helps the steel wire to have better corrosion resistance. To exhibit such actions effectively, the Cu content is preferably 0.05% or more, and more preferably 0.08% or more. In contrast, Cu, if present in an excessively high content, may react with sulfur to be segregated as CuS in a grain boundary region and thereby cause a flaw to be generated during the wire rod manufacturing. To avoid such influence, the Cu content is preferably 0.5% or less, more preferably 0.2% or less, and furthermore preferably 0.18% or less.

[0036] At least one element selected from the group consisting of B in a content of 0.005% or less (excluding 0%), Nb in a content of 0.5% or less (excluding 0%), and V in a content of 0.5% or less (excluding 0%)

[0037] Boron (B) element has actions of preventing the formation of pro-eutectoid ferrite and pro-eutectoid cementite and helping the wire rod to readily control its microstructure to be a homogeneous pearlite. Boron also has actions of fixing, as boron nitride (BN), excess solute nitrogen after the precipitation of AlN, suppressing strain aging caused by the solute nitrogen, and helping the wire rod to have better toughness. In addition, solute boron itself has an action of helping the wire rod to have better toughness. To exhibit such actions effectively, the boron content is preferably 0.0003% or more, more preferably 0.0005% or more, and furthermore preferably 0.001% or more. In contrast, boron, if present in an excessively high content, may cause the precipitation of a compound with iron, i.e., an Fe-B compound such as FeB₂ and cause cracks upon hot rolling. To prevent this, the boron content is preferably 0.005% or less, more preferably 0.004% or less, and furthermore preferably 0.003% or less.

[0038] Niobium (Nb) element forms a nitride with excess solute nitrogen after the precipitation of AlN and contributes to grain refinement. In addition, the element also advantageously fixes solute nitrogen and thereby suppresses aging embrittlement. To exhibit such actions effectively, the Nb content is preferably 0.01% or more, more preferably 0.03% or more, and furthermore preferably 0.05% or more. However, Nb, if present in an excessively high content, may exhibit saturated effects, thus being economically useless. To prevent this, the Nb content is preferably 0.5% or less, more preferably 0.4% or less, and furthermore preferably 0.2% or less.

[0039] Vanadium (V) element forms a nitride with excess solute nitrogen after the precipitation of AlN and contributes to grain refinement, as with Nb. In addition, vanadium also fixes solute nitrogen and thereby suppresses aging embrittlement. To exhibit such actions effectively, the vanadium content is preferably 0.01% or more, more preferably 0.02% or more, and furthermore preferably 0.03% or more. However, vanadium, if present in an excessively high content, may exhibit saturated effects, thus being economically useless. To prevent this, the vanadium content is preferably 0.5% or less, more preferably 0.4% or less, and furthermore preferably 0.2% or less.

[0040] A regular wire rod (referring to one before cold wire drawing) can be manufactured generally by preparing a steel ingot having appropriately controlled chemical compositions by ingot-making, and subjecting the ingot to blooming and hot rolling (where necessary, further to a patenting treatment). It should be noted, however, that the wire rod according to the embodiment of the present invention is intended to control the content and particle size distribution of AlN particles appropriately, where the particle size distribution is controlled so that the percentage of AlN particles having a size d_{GM} of 10 to 20 μm be 50% or more (in number percent) in the d_{GM} extreme value distribution of maximum values of AlN particles. For this purpose, it is important to appropriately control the Al and N contents within the above-specified ranges and to appropriately control a thermal hysteresis in a temperature range in which AlN is precipitated.

[0041] In the steel, AlN begins to be precipitated at about 1300°C or lower, precipitated in a larger amount with a falling temperature, and completely precipitated at about 900°C. During manufacturing processes, blooming and hot rolling processes significantly affect the precipitation behavior of AlN because the steel is exposed to temperatures within the above-mentioned ranges in these processes. Accordingly, blooming and hot rolling conditions should be appropriately controlled. In general, cooling after blooming is performed at a low cooling rate and thereby often causes precipitated AlN particle to coarsen. In contrast, cooling after hot rolling is performed at a relatively high cooling rate and thereby allows precipitated AlN particles to be fine.

[0042] Specifically, blooming may be performed at a heating temperature of 1230°C to 1280°C and a cooling rate of 0.2°C/second or more. Blooming, when performed at a high heating temperature and at a high cooling rate, can prevent precipitation and coarsening of AlN particles. For this reason, the blooming temperature is preferably 1230°C or higher, and more preferably 1240°C or higher. In contrast, blooming, if performed at an excessively high heating temperature, may cause quenching cracks. To prevent this, the blooming temperature is preferably 1280°C or lower, and more preferably 1270°C or lower in terms of its upper limit. The cooling rate is preferably 0.2°C/second or more, more preferably

0.4°C/second or more, and furthermore preferably 0.5°C/second or more. The cooling rate is not limited in its upper limit, but is typically 1.5°C/second or less, and preferably 1.2°C/second or less.

[0043] A billet obtained by blooming is hot-trolled, cooled down to 850°C to 950°C typically by water cooling, and placed in the form of a coil. Fine AlN particles (having a d_{GM} of 10 to 20 μm) can be precipitated by placing the coil-form wire rod at a relatively low temperature. For this reason, the placing temperature is preferably 950°C or lower, more preferably 940°C or lower, and furthermore preferably 920°C or lower. In contrast, placing, if performed at an excessively low temperature, may cause very fine AlN particles to be precipitated in a large number, where such very fine AlN particles do not contribute to hydrogen trap. To prevent this, the placing temperature is preferably 850°C or higher, more preferably 870°C or higher, and furthermore preferably 890°C or higher.

[0044] The content and particle size distribution of AlN particles may be not appropriately controllable typically when at least part of the blooming and hot rolling conditions does not meet the above-specified conditions. In this case, it is also effective to perform a patenting treatment in an appropriate temperature range after hot rolling. The patenting treatment is preferably performed at a re-heating temperature of 880°C to 1000°C and a patenting temperature of 530°C to 620°C. If the work after hot rolling has a low AlN content, the re-heating temperature may be set to be relatively low (e.g., about 880°C to about 940°C) so as to increase the amount of AlN precipitation. If the work after hot rolling includes coarsened AlN particles, the re-heating temperature may be set to be relatively high (e.g., 940°C to 1000°C) so as to allow the coarsened AlN particles to be once dissolved in the steel and to be precipitated again.

[0045] The wire rod according to the embodiment of the present invention sufficiently includes AlN particles capable of effectively acting as hydrogen trap sites, can thereby give steel wires such as wire ropes and prestressing steel wires having excellent delayed fracture resistance, and are useful. The present invention, in another aspect, also includes such steel wires.

Examples

[0046] The present invention will be illustrated in further detail with reference to several working examples below. It should be noted, however, that the examples are by no means intended to limit the scope of the invention; that various changes and modifications can naturally be made therein without deviating from the spirit and scope of the invention as described herein; and all such changes and modifications should be considered to be within the scope of the invention.

[0047] Steel ingots having chemical compositions given in Table 1 were subjected to blooming, hot rolling, and processing into wire rod coils, and some of them were further subjected to a patenting treatment under conditions given in Table 2. Samples were sampled from the resulting works and subjected to an extraction residue measurement to determine the total content of AlN particles and to cross-section observation to evaluate the distribution of AlN particles. The results are indicated in Table 2.

1. AlN Total Content and Solute Nitrogen Content Measurements

[0048] An electrolytic extraction residue measurement with a 10% acetylacetone solution using a 0.1- μm mesh was performed as the extraction residue measurement, in which the amount of AlN particles in the residue was measured by the bromoester method. Independently, the solute nitrogen content was determined by measuring the content of nitrogen compounds including AlN by indophenol absorption spectrophotometry and subtracting the content from the total nitrogen content in the steel. The sample weights were 3 g in the bromoester method and 0.5 g in the absorption spectrophotometry.

2. AlN Distribution Measurement

[0049] The measurement was performed in the following manner. A sample was cut out from each wire rod in a cross section including the wire rod axis and being in parallel to the wire rod longitudinal direction so that the total area of two areas from the surface layer to a position of one-fourth ($D/4$) the diameter D of the wire rod be 140 mm^2 . Specifically, the length L of the sample was determined so that $L \times D/4 + L \times D/4 = L \times D/2$ be 140 mm^2 . The size of an AlN particle having the maximum size in an observation view field in the cross section was measured according to JIS G0555, and this measurement was performed in arbitrary twenty (20) view fields. In the measurement, Group D and Group DS inclusions as specified in JIS G0551 were regarded as AlN particles, and the geometrical mean $(ab)^{1/2}$ of the length (a) and thickness (b) of each AlN particle was employed as the size of the AlN particle.

[0050] Next, the above-obtained wire rod coils were subjected to wire drawing to give steel wires, and the tensile strength (wire strength) of each steel wire was measured. The steel wires were further subjected to stranding and hot stretching to give strands having strand diameters and strand structures as given in Table 2, and the rope strength, delayed fracture resistance, and twisting properties of each strand were measured. The results are indicated in Table 3.

3. Steel Wire Tensile Strength (Wire Strength) Measurement

[0051] The tensile strength of each steel wire was measured according to JIS Z2241.

4. Rope Strength Measurement

[0052] As the rope strength, the maximum force of a sample in a tensile test was measured according to JIS G3536.

5. Delayed Fracture Resistance Measurement

[0053] The delayed fracture property (delayed fracture resistance) was measured in the following manner. Each of twelve (12) samples was immersed in a 20 percent by mass ammonium thiocyanate solution at 50°C under a load of 0.8 p.u according to the description in Literature 1 (fib Bulletin No. 30: Acceptance of stay cable systems using prestressing steels, January 2005), and a time period until the sample was broken was measured. The term "0.8 p.u" refers to a load of 80% of a breaking load. A test sample having a minimum rupture time of 2 hours or longer and a median rupture time of 5 hours or longer was accepted herein.

6. Twisting Properties Measurement

[0054] For the twisting properties, a test sample having a twisting number of 3 or more (capable of twisted three times or more) according to FKK HTS-26 Standard of the FKK Freynessit system was accepted herein.

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50
55

Steel type	Chemical composition (in mass percent) *with the remainder being iron and inevitable impurities														Upper limit of Al content (right-hand value of Expression (1))	
	C	Si	Mn	N	Al	P	S	Cr	Cu	Co	Mo	Ni	Nb	V		B
A	0.92	1.18	0.48	0.0040	0.06	0.010	0.010	0.19								0.17
B	0.80	0.61	0.51	0.0025	0.10	0.011	0.006									0.20
C	0.90	1.19	0.50	0.0053	0.06	0.008	0.008									0.14
D	0.86	1.21	0.71	0.0080	0.05	0.010	0.010						0.09			0.09
E	1.05	0.30	1.78	0.0032	0.07	0.010	0.011									0.19
F	0.92	0.81	0.51	0.0020	0.06	0.007	0.010		0.08			0.28				0.21
G	0.84	1.82	0.20	0.0061	0.12	0.010	0.020								0.0048	0.13
H	0.92	1.10	0.48	0.0048	0.07	0.020	0.008	0.28							0.0028	0.15
I	0.90	0.89	0.81	0.0068	0.09	0.007	0.010								0.0039	0.11
J	1.20	0.40	0.49	0.0096	0.05	0.008	0.012			0.18	0.08		0.07			0.05
K	0.85	0.58	0.61	0.0042	0.13	0.006	0.008									0.17
L	1.30	0.79	0.51	0.0072	0.08	0.010	0.007									0.10
M	0.70	1.32	0.81	0.0036	0.10	0.015	0.011									0.18
N	0.93	0.71	0.60	0.0028	0.03	0.010	0.010									0.20
O	1.10	0.38	0.81	0.0029	0.17	0.008	0.013									0.19
P	0.85	0.39	0.68	0.0010	0.07	0.010	0.010									-
Q	0.90	0.40	0.58	0.0120	0.06	0.008	0.011									-
R	0.96	0.61	0.59	0.0090	0.11	0.008	0.011									0.07
S	0.96	1.20	0.30	0.0050	0.08	0.008	0.010							0.10		0.06

[Table 2]

Test number	Steel type	Bloom		Hot rolling		Patenting		Microstructure	Solute nitrogen content (ppm)	AIN content (ppm)	AIN distribution
		Bloom temperature (°C)	Cooling rate (°C/s)	Placing temperature (°C)	Rolled wire diameter (mm)	Heating temperature (°C)	Patenting temperature (°C)				
1	A	1260	0.5	950	18.0	-	-	P	15	73	○
2	B	1240	0.8	850	16.0	-	-	P	3	64	○
3	C	1260	0.4	900	14.0	-	-	P	12	120	○
4	C	1200	0.4	900	14.0	-	-	P	5	140	×
5	C	1260	0.5	950	14.0	960	550	P	11	121	○
6	C	1250	0.1	900	14.0	-	-	P	3	150	×
7	C	1230	0.5	1050	14.0	-	-	P	13	37	×
8	C	1280	0.6	750	14.0	-	-	P	11	113	×
9	C	1280	0.8	940	14.0	-	-	P	30	62	○
10	C	1250	0.5	1000	14.0	970	570	P	12	113	○
11	C	1300	0.5	Quenching cracks developed upon blooming							
12	C	1260	0.5	900	14.0	900	500	P+B	9	118	○
13	D	1260	0.5	800	16.0	880	590	P	2	72	○
14	E	1250	0.5	850	14.0	910	540	P	5	64	○
15	F	1240	0.5	820	12.0	930	550	P	2	53	○
16	G	1280	0.8	850	10.0	940	610	P	6	161	○
17	H	1260	0.7	800	6.0	940	570	P	1	138	○
18	I	1270	0.5	850	5.5	1000	590	P	2	223	○
19	J	1260	0.5	900	7.0	940	540	P	1	69	○
20	K	1250	0.5	900	8.0	950	550	P	1	106	○
21	L	1250	0.5	900	14.0	960	550	P	11	174	○
22	M	1260	0.5	870	12.0	960	620	P	3	97	○

(continued)

Test number	Steel type	Blooming		Hot rolling		Patenting		Microstructure	Solute nitrogen content (ppm)	AIN content (ppm)	AIN distribution
		Blooming temperature	Cooling rate	Placing temperature	Rolled wire diameter	Heating temperature	Patenting temperature				
23	N	1240	0.5	880	13.0	960	560	P	12	47	○
24	O	1250	0.5	880	8.0	960	530	P	4	65	○
25	P	1250	0.5	820	13.0	960	580	P	3	12	×
26	Q	1260	0.5	820	13.0	960	580	P	40	206	×
27	R	1250	0.5	850	13.0	960	580	P	6	165	×
28	S	1250	0.5	880	8.0	950	580	P	8	123	○

[Table 3]

Test number	Steel type	Wire strength (MPa)	Strand diameter (mm)	Strand structure	Maximum force (kN)	Minimum rupture time (hour)	Median rupture time (hour)	Number of twisting (time)		Remarks
1	A	2240	15.2	7-wire	346	2.5	5.3	31		High strength
2	B	2169	15.2	7-wire	335	3	5.2	29		
3	C	2176	15.2	7-wire	336	2.3	5.8	32		
4	C	2143	15.2	7-wire	331	0.6	2.5	26		
5	C	2137	15.2	7-wire	330	3.1	6.3	28		
6	C	2130	15.2	7-wire	329	0.5	2.7	21		
7	C	2143	15.2	7-wire	331	0.7	2.5	22		
8	C	2169	15.2	7-wire	335	0.5	2.7	21		
9	C	2169	15.2	7-wire	335	2.2	6.3	8		
10	C	2182	15.2	7-wire	337	3.5	6.8	26		
11	C									
12	C				Numerous breaks developed upon wire drawing					
13	D	2272	12.7	7-wire	231	3.5	6.8	26		Good ductility
14	E	2213	12.7	7-wire	225	2.2	6.2	38		
15	F	2207	21.8	19-wire	667	9	14.2	46		Large twisting number
16	G	2187	21.8	19-wire	661	4	5.9	51		Large twisting number
17	H	2116	28.6	19-wire	1062	3.2	6.1	48		High strength and large twisting number
18	I	2090	28.6	19-wire	1049	3.5	5.6	47		Large twisting number
19	J	2111	15.2	7-wire	326	10	15.7	28		Good ductility
20	K	2040	15.2	7-wire	315	11	16.3	25		
21	L				Numerous breaks developed upon wire drawing					
22	M	1823	15.2	7-wire	257	-	-	-		-
23	N	2046	15.2	7-wire	316	0.6	2.6	26		

(continued)

Test number	Steel type	Wire strength (MPa)	Strand diameter (mm)	Strand structure	Maximum force (kN)	Minimum rupture time (hour)	Median rupture time (hour)	Number of twisting		Remarks
									(time)	
24	O	Numerous breaks developed upon wire drawing								
25	P	1998	28.6	19-wire	1003	0.4	3.1	31		
26	Q	2096	28.6	19-wire	1052	1.4	4.3	2		
27	R	2197	28.6	19-wire	1103	0.6	3.6	16		
28	S	2194	21.8	19-wire	663	2.5	5.4	34		

[0055] Test Nos. 1 to 3, 5, 9, 10, and 13 to 20 had chemical compositions, microstructures, AlN contents, and AlN distributions respectively meeting the conditions specified in the present invention, thereby achieved a wire strength of 2000 MPa or more (preferably 2100 MPa or more), offered such a high strand strength as to meet a criterion prescribed in JIS G3536, still had good delayed fracture resistance, and could give high-strength strands that are practically workable.

In addition, these test samples also met the condition for solute nitrogen content and thereby offered excellent twisting properties. Of the samples according to the embodiment of the present invention, Test Nos. 15 to 18 were samples particularly having a reduced solute nitrogen content and thereby offered very excellent twisting properties; whereas Test No. 9 had a highest solute nitrogen content and offered a smallest number of twisting among the samples according to the embodiment of the present invention.

[0056] Test Nos. 10, 15, and 17 underwent hot rolling performed at a placing temperature out of the range of preferred condition, but underwent an appropriate patenting treatment thereafter, and could give wire rods meeting the conditions specified in the present invention.

[0057] In contrast, Test Nos. 4, 6 to 8, 11, 12, and 21 to 27 were samples that failed to meet any of the conditions specified in the present invention or were manufactured under a condition not meeting the manufacturing conditions required for obtaining steels according to the embodiment of the present invention.

[0058] Test No. 4 underwent blooming performed at a low heating temperature; and Test No. 6 underwent cooling performed at a low cooling rate after blooming. These samples each suffered from precipitation of coarse AlN particles, had an AlN particle size distribution not meeting the condition specified in the present invention, and offered inferior delayed fracture resistance.

[0059] Test No. 7 underwent placing performed at an excessively high temperature after hot rolling, suffered from insufficient precipitation of AlN particles during placing, had an AlN content and an AlN particle size distribution both not meeting the conditions specified in the present invention, and offered inferior delayed fracture resistance. Test No. 8 underwent placing performed at an excessively low temperature after hot rolling, suffered from excessive refinement of AlN particles, thereby had an AlN particle size distribution not meeting the condition specified in the present invention, and offered inferior delayed fracture resistance.

[0060] Test No. 11 underwent blooming performed at an excessively high heating temperature and suffered from quenching cracks.

[0061] Test No. 12 underwent a patenting treatment performed at an excessively low temperature, thereby had a microstructure including a mixture (P+B) of bainite (B) and pearlite (P) phases, and offered inferior wire drawability. This sample had a bainite fraction of about 20 percent by area.

[0062] Test No. 21 was a sample having an excessively high carbon content, underwent significant aging embrittlement during wire drawing, and suffered from numerous breaks. Test No. 22 was a sample having an excessively low carbon content and failed to offer a strength corresponding to strand B type as prescribed in JIS G3536.

[0063] Test No. 23 was a sample having an excessively low Al content, failed to include AlN particles in a sufficient amount, and offered inferior delayed fracture resistance. Test No. 24 was a sample having a nitrogen content within the range specified in the present invention but being relatively low and having an excessively high Al content, suffered from the formation of Al-containing oxides in a large amount, and suffered from numerous breaks upon wire drawing.

[0064] Test No. 25 was a sample having an excessively low nitrogen content, failed to include AlN particles in a sufficient amount, had an AlN particle size distribution not meeting the conditions specified in the present invention, and offered inferior delayed fracture resistance. Test No. 26 was a sample having an excessively high nitrogen content, suffered from the precipitation of coarse AlN particles, and thereby offered inferior delayed fracture resistance. Test No. 26 had a solute nitrogen content not meeting the preferred condition in the present invention and had a smallest number of twisting among the entire test samples.

[0065] Test No. 27 was a sample having a nitrogen content within the range specified in the present invention, but being relatively high, and having an Al content not meeting the condition specified by Expression (1), suffered from the precipitation of coarse AlN particles, and offered inferior delayed fracture resistance.

Claims

1. A wire rod comprising:

C in a content of 0.8% to 1.2% (in mass percent, hereinafter the same for chemical composition);

Si in a content of 0.1% to 2.0%;

Mn in a content of 0.1% to 2.0%;

N in a content of 0.002% to 0.010%;

Al in a content of 0.04% to 0.15%;

P in a content of 0.02% or less (including 0%); and

S in a content of 0.02% or less (including 0%),
with the remainder being iron and inevitable impurities;
the Al content and N content meeting a condition specified by Expression (1) given as follows:

$$[Al] \leq 2.1 \times 10 \times [N] + 0.255 \quad (1)$$

where [Al] and [N] are contents (in mass percent) of Al and N, respectively;
the wire rod having a microstructure comprising 95 percent by area or more of a pearlite;
the wire rod having a content of AlN of 0.005% or more; and
a percentage of AlN particles having a diameter d_{GM} of 10 to 20 μm being 50% or more in number percent in
an extreme value distribution of maximum values of the diameters d_{GM} of AlN particles, where the diameter
 d_{GM} is represented by a geometrical mean $(ab)^{1/2}$ of a length "a" and a thickness "b" of an AlN particle.

2. The wire rod according to claim 1, having a solute nitrogen content of 0.003% or less.

3. The wire rod according to claim 1, further comprising at least one element selected from the group consisting of:

Cr in a content of 1.0% or less (excluding 0%);
Ni in a content of 1.0% or less (excluding 0%);
Co in a content of 1.0% or less (excluding 0%);
Mo in a content of 1.0% or less (excluding 0%); and
Cu in a content of 0.5% or less (excluding 0%).

4. The wire rod according to claim 1, further comprising at least one element selected from the group consisting of:

B in a content of 0.005% or less (excluding 0%);
Nb in a content of 0.5% or less (excluding 0%); and
V in a content of 0.5% or less (excluding 0%).

5. A steel wire obtained from the wire rod of any one of claims 1 to 4.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/058566

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00 (2006.01) i, C22C38/06 (2006.01) i, C22C38/58 (2006.01) i, C21D8/06 (2006.01) n, C21D9/52 (2006.01) n

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)

C22C1/00-49/14, C21D8/06, C21D9/52

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2013
Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/001057 A1 (Nippon Steel Corp.), 04 January 2007 (04.01.2007), & JP 2007-39800 A & US 2009/0229711 A1 & EP 1897964 A1 & CN 101208446 A & KR 10-2008-0017465 A & KR 10-0995160 B	1-5
A	JP 2008-261027 A (Nippon Steel Corp.), 30 October 2008 (30.10.2008), (Family: none)	1-5
A	JP 2009-280836 A (Nippon Steel Corp.), 03 December 2009 (03.12.2009), (Family: none)	1-5

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search
06 June, 2013 (06.06.13)

Date of mailing of the international search report
18 June, 2013 (18.06.13)

Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/058566

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/089782 A1 (Nippon Steel Corp.), 28 July 2011 (28.07.2011), & JP 4842408 B & CN 102292460 A & KR 10-2011-0099749 A	1-5
A	JP 2012-41587 A (Nippon Steel Corp.), 01 March 2012 (01.03.2012), & WO 2012/023483 A1	1-5

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REFERENCES CITED IN THE DESCRIPTION

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